

REDUCTION OF TANNERY WASTE VOLUME THROUGH COUNTERCURRENT REUSE OF PROCESS STREAMS*

M. KOMANOWSKY

AND

G. E. SENSKE

*Eastern Regional Research Center†
Philadelphia, Pennsylvania 19118*

Abstract

Tannery effluents are expensive to treat — biologically because of their high waste loads and physiochemically because of their large volumes. Countercurrent reuse of all prechrome processing streams in a manner similar to classical multistage leaching drastically reduced the effluent volume generated in the preparation of hides for tanning (to between 1/10 and 1/20 of the present volume). Pretreatment of process streams was limited, consisting only of ammonia recovery from the bating solution, sludge separation from the unhairing effluent, and pH adjustment of the post-relime and post-bate wash waters. The resulting leathers were comparable in physical strength and visual appearance to those made conventionally, although they had a slightly less uniform coloration when dyed than conventionally produced leather. This problem was partially eliminated by adding detergent, and by increased mechanical action. This report contrasts countercurrent with conventional processing in terms of the chemical composition of the hides and of the effluents at corresponding processing stages. The benefits derived from this processing approach with regard to pollution are also discussed.

Introduction

As more accurate research data are accumulated on tannery waste treatment, it is becoming increasingly obvious that pollution abatement would be very expensive if tanners were forced to meet the strict effluent limitations originally proposed by EPA. The principal causes for the high cost of tannery waste treatment are the large effluent volume, the high pollution load, and the disproportionate

*Presented at 77th Annual Meeting of the American Leather Chemists Association, Sea Pines Plantation, Hilton Head Island, S.C., June 15, 1981.

†Agricultural Research Service, U.S. Department of Agriculture.

content of poorly degradable protein nitrogen. According to the June 1973 report to the EPA by Stanley Consultants (1), which gives the costs at 1971 price levels, a typical U.S. side leather tannery, processing 1,000 hides and emitting 965 cu m effluent per day, would have to pay \$662,000 per year for waste pretreatment which would include activated sludge and nitrification/denitrification. Now, 10 years later, the costs are about 2.2 times higher. The report shows also that for the same cost, 90 cu m of effluent from a hide-curing operation can be treated by a cost-intensive method such as evaporation. Clearly, reduction of tannery effluent to 1/10 its present volume would yield a promising solution to the waste treatment problem of U.S. tanneries. Because these wastes have a relatively low salt content, they could, unlike brine, be treated at a fraction of the cost, using more conventional waste treatment methods.

Our research findings (2) indicate that a combination of physiochemical and biological methods provides the cheapest and the most reliable approach for treating tannery waste. But, with large volumes, this approach is still almost as prohibitive as the principally biological treatment alternatives proposed by the EPA. If the effluents can be reduced to 1/10 their present volumes, however, physiochemical treatments become very attractive. They are very compact and relatively cheap. They yield byproducts that might be sold and reused to recoup some of the treatment costs. And most importantly, their sale would lower the solid waste disposal charges which are expected to rise dramatically in the near future because of stricter land-fill regulations. As long as treatment costs are prohibitive, it is meaningless to speak of recovering some of them, but as they are lowered, the sale of byproducts and reduction of waste disposal charges begin to significantly offset the total treatment expense.

The potential for savings offered by volume reduction was recognized early by tanners as the waste problem became more acute. They upgraded their equipment and processing procedures to decrease the float volumes to a minimum. Recycling of effluents would have been a further step in that direction, but tanners have been wary of introducing recycling into their commercial processing because they have felt that the limited reduction in effluent volume thus obtained is not worth the unstable operating conditions created which can interfere with consistent production of high-quality leather.

On the other hand, the more extensive countercurrent reuse of effluents reported in this paper offers both worthwhile reduction in effluent volume and stability in operating conditions, once equilibrium has been established. Therefore, it has the potential of greatly reducing the cost of tannery waste treatment.

Processing Method

In the countercurrent processing scheme studied in this work, hides were loaded into the hide processor or drum and exposed to different solutions for predeter-

mined lengths of time just as in the processes now used commercially. However, the effluents from each operation or processing stage were not discarded as is usually done. Instead, they were stored in separate storage tanks and reused in the subsequent run, although not in the same but in the preceding operating stage. For example, the relime effluent became the unhairing solution, while the unhairing effluent became the soak of the next run, and so forth. Theoretically this mode of processing is identical to continuous countercurrent leaching by stages.

The countercurrent reuse procedure can be seen from the flow diagram depicted in Figure 1. Salted hides were subjected to three soaking steps; then unhairing, reliming, and two post-lime washing steps; followed by deliming and bating, and two post-bate washing steps. The subsequent treatments are not shown since they are identical to conventional processing using fresh water. While conventional processing involves the use of fresh water in every step, the countercurrent reuse studied here involved addition of fresh water only once — in post-bate wash 2 (denoted at the bottom of the flow diagram of Figure 1). The effluent from this step (represented by the broken line or arrow of that figure) was reused in a countercurrent mode first in post-bate wash 1, and then in deliming and bating after addition of ammonium sulfate and enzyme. The effluent from the delime/bate step was pretreated before reuse. Lime was added to it and the calcium sulfate formed was centrifuged out while the ammonia was removed either by evaporation or by gas-stripping. This treated effluent was then used in post-relime wash 2 and later in post-relime wash 1, and after addition of calcium hydroxide, in the relime. The relime effluent, in turn, was strengthened with sodium sulfide and used for unhairing. The other effluent which had to be pretreated before reuse was the unhairing solution. It was merely centrifuged to remove suspended solids before being used for soaking: first in soak 3, then in soak 2, and finally in soak 1. The first soak was discarded and this was the only liquid effluent from the pre-chrome processing steps that left the tannery.

As mentioned before, in actual practice the hides were not moved physically from drum to drum or from hide processor to hide processor. Instead, the charge in a drum was treated by a succession of liquids as if it were being moved from stage to stage in a countercurrent system. Between runs the liquids were stored in separate tanks.

Experimental Conditions

Sixteen experiments were conducted in a hide processor (Challenge-Cook Bros., Model HP12*) using four sides per run. The brined Black Angus hides were not removed from it during a run, only the solutions were pumped in and out. The

*Reference to brand or firm name does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

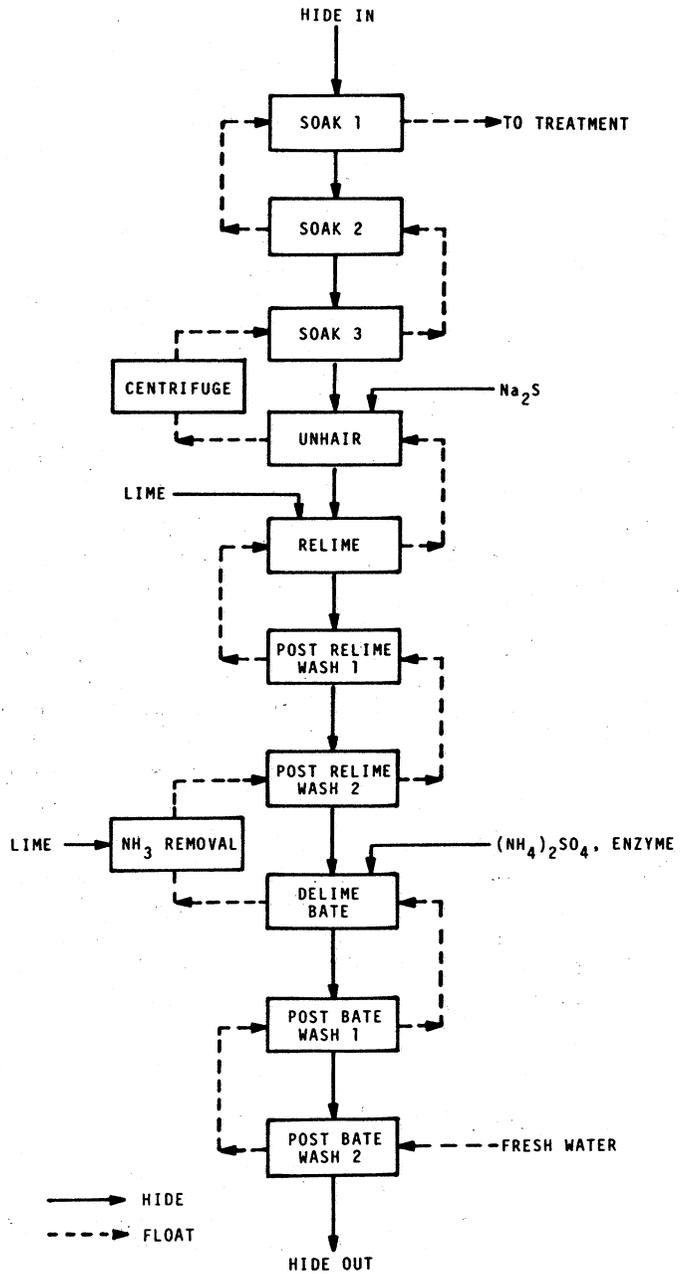


FIGURE 1. — Countercurrent reuse of effluents.

operating conditions and schedules for the countercurrent processing procedure* are outlined below:

Soak 1

Approx. 125 percent float, 85°F — made up from soak 2 (decanted)
Tumble 30 min/hr at 4 rpm for 6 hr
Discarded effluent

Soak 2

Approx. 135 percent float, 85°F — made up from soak 3 (decanted)
Tumble 10 min/hr at 4 rpm overnight

Soak 3

Approx. 140 percent float, 85°F — made up from unhairing solution (centrifuged)
Tumble 30 min/hr at 4 rpm for 5½ hr

Unhairing

Approx. 145 percent float, 85°F — made up from relime + 2 percent Na₂S
Tumble 1 hr on/1 hr off/1 hr on for 3 hr at 4 rpm

Relime

Approx. 150 percent float, 85°F — made up from post-relime wash 1 (decanted) + 2.5 percent lime + fresh water
Tumble 10 min/hr overnight at 4 rpm

Post-relime wash 1

Approx. 135 percent float, 85°F — made up from post-relime wash 2 (decanted) adjusted to pH 7 with HCl
Tumble 60 min/hr for 1 hr at 4 rpm

Post-relime wash 2

Approx. 135 percent float, 90°F — made up from delime/bate (after NH₃ removal, decanting of susp. sol., and pH adjustment to 7 with HCl) + 0.1 percent Triton X-114.
Tumble 60 min/hr at 4 rpm for 1 hr

In the following steps the weight basis was changed to limed hide weight:

Delime/bate

Approx. 100 percent float, 90°F — made up from post-bate wash 1 (after decanting) + 3.3 percent ammonium sulfate + 0.09 percent

* Percentage based on brined hide weight; chemicals on 100 percent basis.

Oropon WN-4
Tumble 60 min/hr for 1¼ hr at 10 rpm
(Maintain pH range 8-9)

Post-bate wash 1

Approx. 100 percent float, 85°F — made up from post-bate wash 2
(after decanting and pH adjustment to pH 4 with H₂SO₄)
+ .1 percent Triton X-114
Tumble 60 min/hr for ½ hr at 10 rpm

Post-bate wash 2

100 percent float, 85°F — fresh water
Tumble 60 min/hr for ½ hr at 10 rpm

Observe that in general the procedure was similar to conventional processing. However, there were three soaking steps instead of the usual presoak or wash, and soak. An additional soak was added to accomplish more efficient salt removal before the hides were unhaired. Soak 2 was carried out overnight for convenience. A 6-hr soak would have been just as satisfactory since equilibrium in salt concentration between the hides and the solution is readily established in that time. Thus, the total soaking time could have been 18 hr with equal results. The float was adjusted to 150 percent in the relime. As the float was reused, ½ was partly absorbed by the hide and partly lost in the centrifuge cakes and in the settled sludges from each stage which were discarded. Thus, the equivalent of a 100 percent float was discharged only in soak 1.

Triton X-114 was added during post-relime wash 2 and post-bate wash 1 to help clean up the hide. The post-relime washes 1 and 2 were adjusted to pH 7 with HCl before the solution was added to the hide processor. (In the future, this awkward pH adjustment will be avoided by using excess ammonium sulfate during bating.)

Fresh water (100 percent float) was added in post-bate wash 2. Since in all the subsequent processing steps standard operating conditions were adhered to, they are not shown.

For comparison, two runs were made at the same operating conditions, except that fresh water was used in every processing step.

All analyses were conducted using standard procedures recommended by ALCA (3), except in the case of calcium, chromium, iron, and sodium which were analyzed by atomic absorption spectroscopy (4), and in the case of chloride which involved ashing prior to analysis by the ALCA procedure (3).

Results and Discussion

Attempts at reuse of tanning liquors date probably as far back as the art of making leather itself. As a matter of fact, it was customary at one time to use old

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Tumble 60 min/hr for 1¼ hr at 10 rpm
(Maintain pH range 8-9)

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+ .1 percent Triton X-114

Tumble 60 min/hr for ½ hr at 10 rpm

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lime liquors, at least in the first of a series of liming steps in which progressively fresher lime liquors were used. While the older lime liquors speeded up the unhairing process, they often yielded variable results. To accelerate the unhairing process even more and to assure uniform product quality, sharpening agents, mostly sodium sulfide, became preferable and reuse of unhairing and lime liquors lost its popularity.

However, tannery effluents other than lime liquors and tanning liquors were usually not reused. The main reasons for the limited adaptability of tannery liquors for reuse were summarized in 1948 by Bowes (5), who stated that "reuse of liquors will lead to the accumulation of salts, soluble nitrogen, etc., in the liquors and must therefore make for lack of uniformity from pack to pack. Examination of lime liquors and pelts from a number of trade liming processes indicates that one mend can satisfactorily be carried out without detriment to the fiber structure; further mending, however, is probably undesirable." Note that Bowes blamed the variability of salt content and not the salt concentration *per se* for the lack of uniformity. As a matter of fact, Bowes suggested that the important actions involved in liming and the factors affecting them can be controlled by a proper balance of the various constituents of lime liquors. Table I, which was excerpted from the paper by Bowes, shows that hydroxyl and sulfide ions have the effect of increasing

TABLE I
CONTROL OF ACTION^a INVOLVED IN UNHAIRING

Action	Constituent					Soluble nitrogen
	OH ⁻	S ²⁻	Ca ⁺⁺	Na ⁺	Salts	
Unhairing	↑	↑	-	-	↑	↑
Chemical action on collagen	↑	-	-	-	-	↑
Plumping	↑	-	↑	↑	↑	↑
Opening up (Decreased cohesion)	↑	↑	↑	-	↑	↑
Splitting up of fibers	-	↑	↑	-	↑	↑

^aUpward arrows indicate enhancement; downward arrows indicate decrease of action.

the various physical and chemical actions on the proteins (such as hair destruction, and swelling and opening up of the hide, as well as splitting up of collagen fibers). However, the presence of larger amounts of salt has just the opposite effect and may be used to counterbalance and control the effect of the ions on the hair and hide proteins. In this table, an arrow pointing up indicates that an increase in concentration of an ion will increase the action listed in the first column, and an arrow pointing down, that such an increase in concentration will decrease the

action. Of course, the salt effect is much more complicated than shown in this table but the table is sufficiently accurate to serve as a general, qualitative guide for controlling unhairing and reliming operations. Studies of the effect of adding different amounts of inorganic chemicals such as lime, sodium sulfide, calcium chloride, and sodium chloride on weight gain, swelling, and plumping during liming, have been reported in 1964 by Herfeld (6) in a series of six papers which clarify and support the ideas expressed in Table I using quantitative data. As a matter of fact, the table seems to be in general agreement with the liming procedures developed in the last two decades by Herfeld (6), Van Vlimmern (7), and Sharp-house (8). They all divide liming into two phases. In the first phase, unhairing is effected using high concentrations of OH^- , S^- , and either very high salt contents or very low quantities of water to prevent swelling and plumping. In the second phase, water is added to drop the concentration of salt and chemicals and thereby enhance swelling and opening up of the hide structure.

Whether old or new, all successful commercial processes nowadays are conducted under uniform conditions from run to run. Starting with a batch of hides containing a known amount of salt, predetermined amounts of water and chemicals are added and reacted with the hides for a predetermined amount of time, using accurately controlled stable operating conditions. The recycling processes recently published by Davis and Scroggie (9) Vulliermet (10), and others cannot maintain constant operating conditions from batch to batch and guarantee product uniformity unless provisions are made to prevent buildup of fats and pigment matter (e.g., by filtration) and enough water is used during soaking to prevent carryover of salt into the unhairing liquor (11). If an effluent, such as an unhairing solution, is brought into contact with an insufficiently soaked batch of hides, it will pick up salts and hair proteins from it. Even if suspended solids are then removed from that effluent, its soluble solids content will be different and hence it will have a different action on the next batch of hides. This is probably the reason why these published recycling procedures have not been readily accepted and put into commercial use.

Unlike the published recycling procedures, the countercurrent reuse of effluents reported here is inherently self-stabilizing and, therefore, can guarantee stable conditions after equilibrium is attained. This is most readily seen from Figure 2, which gives the final sodium ion concentration and the NaCl concentration in each processing stream. Of course, the salt concentration is lower in the conventional fresh water run depicted by the broken line than in the two USDA experimental runs represented by the solid lines. It is noteworthy that the solid curves are close together showing that at equilibrium, the conditions do indeed stabilize and remain the same from run to run. It should be noted that by the tenth step (the post-bate wash 2), the salt concentrations of the USDA experimental runs have decreased almost to the same level as that of the conventional fresh water run even though only 1/10 the amount of water had been used in the former.

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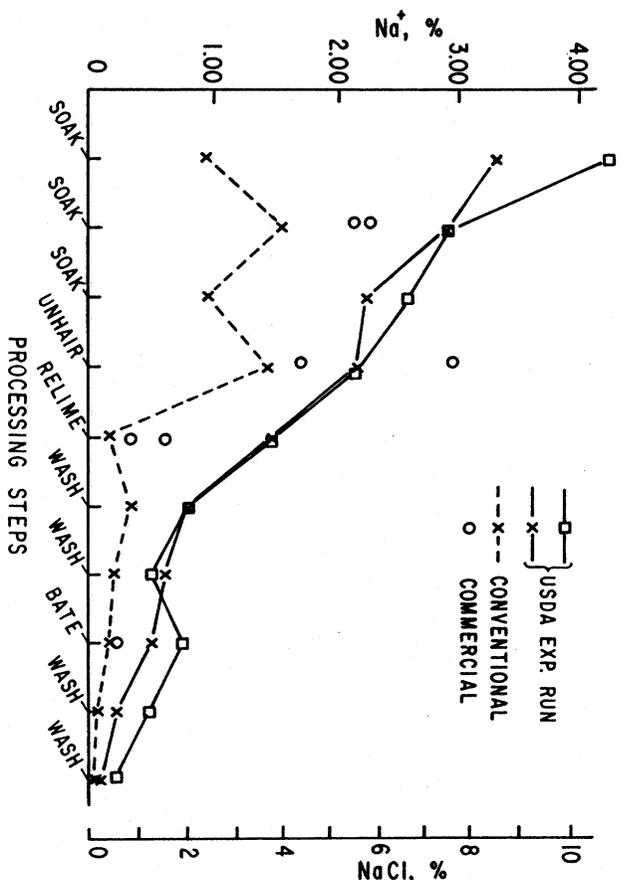


FIGURE 2. — Sodium content in effluent streams.

In the fresh water or conventional run denoted by the broken line, the salt is discarded from the process with the effluent from each stream. The sum of the salt contents of all the discarded streams is equal to about 13 to 14 percent, the approximate salt content of the hide.

On the other hand, in the countercurrent reuse runs denoted by solid lines, the salt diffusing out of the hide in each step is cumulative since the effluent is not discarded and consequently the salt content builds up to 10 percent in the effluent from soak 1. It would have been even higher, or 13 or 14 percent, if some of that salt had not been lost during pretreatment prior to reuse of the unhairing and bating streams.

The concentration of salt in the reliming bath of the countercurrent process is also very significant. In 1948, Bowers (5) expressed the opinion that lime liquors probably should not contain more than 2 to 3 percent salt. In the countercurrent process using 150 percent float in the relime, the salt content is 1-1½ times the optimum recommended by Bowers, or about 3.8 percent. However, should it become evident that further decrease in salt content is desirable in the reliming step of the countercurrent process, a decrease can readily be achieved by raising the

percent float slightly or by increasing the number of rinsing steps used. However, the need for decreasing the sodium content depends on the desired leather properties. Some shoe upper leather manufacturers intentionally add salt to above 2 percent, having learned that at these higher concentrations, swelling and plumping is decreased but enough opening up of the fiber is attained to result in softer, spongier leather (12).

Following the countercurrent flow of the water further, one observes that the salt concentration increases in the unhairing step to 5.6 percent. (Actually, 0.79 percent sodium ions were added in this step in the form of sodium sulfide to the 1.5 percent which were already there, yielding a total of 2.29 percent sodium ions. This reduced the difference in sodium ion concentration between the hide and the solution sufficiently to slow down diffusion of salt out of the hide in this step.) It can be argued that 5.6 percent sodium chloride is too high for unhairing but the authors observed no problems in unhairing at this salt concentration. Besides, some commercial unhairing solutions are in that range as can be seen from the points in the diagram represented by the circles. And Slabbert (11) recently reported no problems in unhairing at salt contents below 8 percent.

Finally, examination of the sodium chloride content in the three soaking steps reveals that they contain about 5.8, 7.4, and 9.5 percent in soaks 3, 2, and 1,

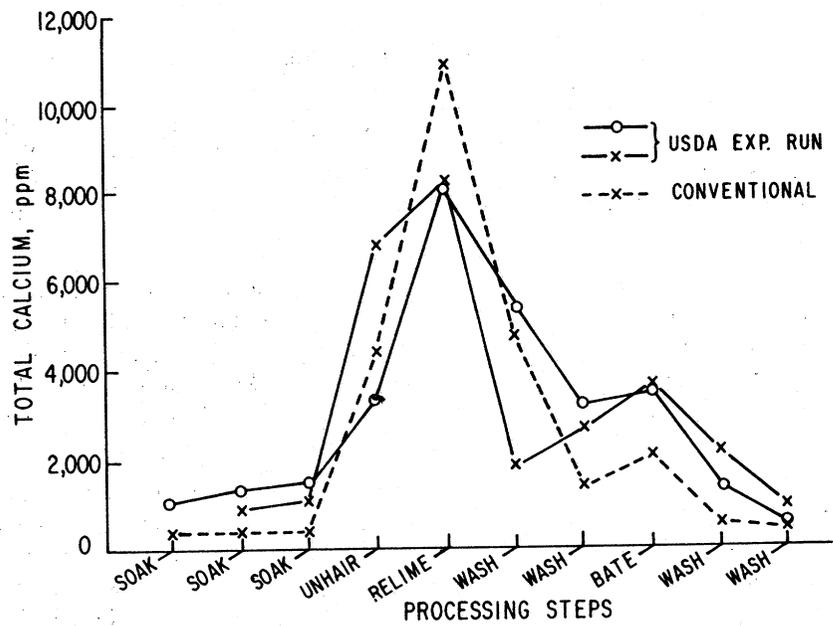


FIGURE 3. - Total calcium content in effluent streams.

respectively. This corresponds to the range in salt concentration reported in the literature to be most effective in the removal of interfibrillary proteins.

Thus, examination of the sodium ion concentration in each of the ten steps of the countercurrent effluent reuse process reveals not only that stable conditions are attained in that process but also that the sodium ion concentration is within limits considered acceptable by commercial standards.

From the proximity of the two solid lines for the countercurrent process and the broken line for the conventional process in Figure 3, it can be concluded that the countercurrent process is stable and practically identical to the conventional process with respect to the concentration of calcium ions in each of the processing steps. This is true also with respect to ammonia (Figure 4) and sulfide (Figure 5).

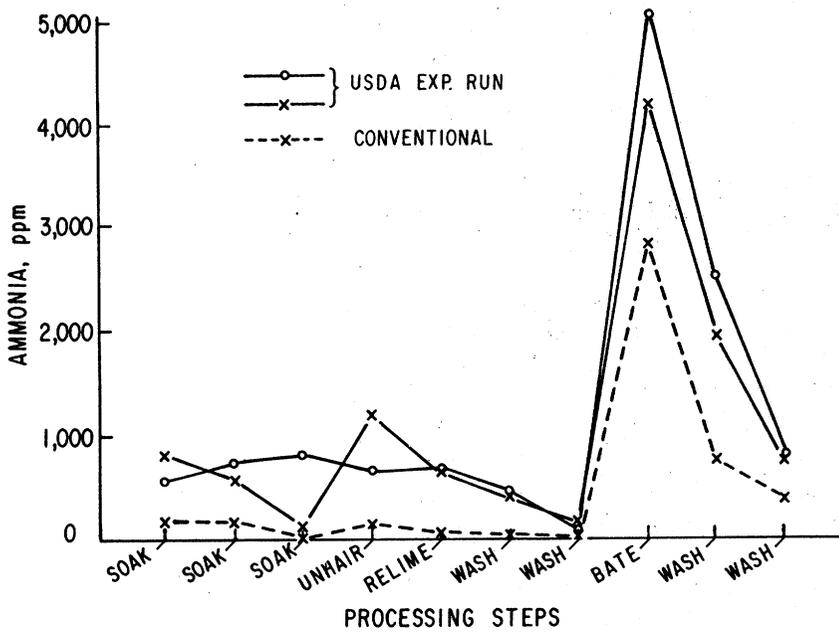


FIGURE 4. — Ammonium content of effluent streams.

The reason for the sharp drop in sulfide in the three soaking steps in Figure 5 requires additional study. Some of it probably reacted with the incoming hide and the rest was oxidized during the soaking steps and during storage between runs. When the calcium, the ammonia, and the sulfide concentration in each step of the countercurrent process is compared with the corresponding values of the conventional process, it is readily seen that the differences are small and probably insignificant.

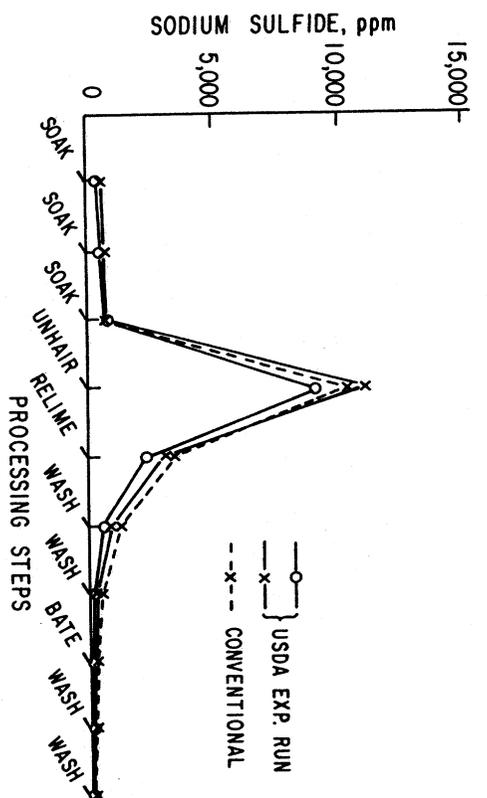


FIGURE 5. — Sodium sulfide content in effluent streams.

Figure 6 shows that the two types of processes exhibit a minor deviation with respect to the total Kjeldahl nitrogen (TKN) distribution. The TKN curve has

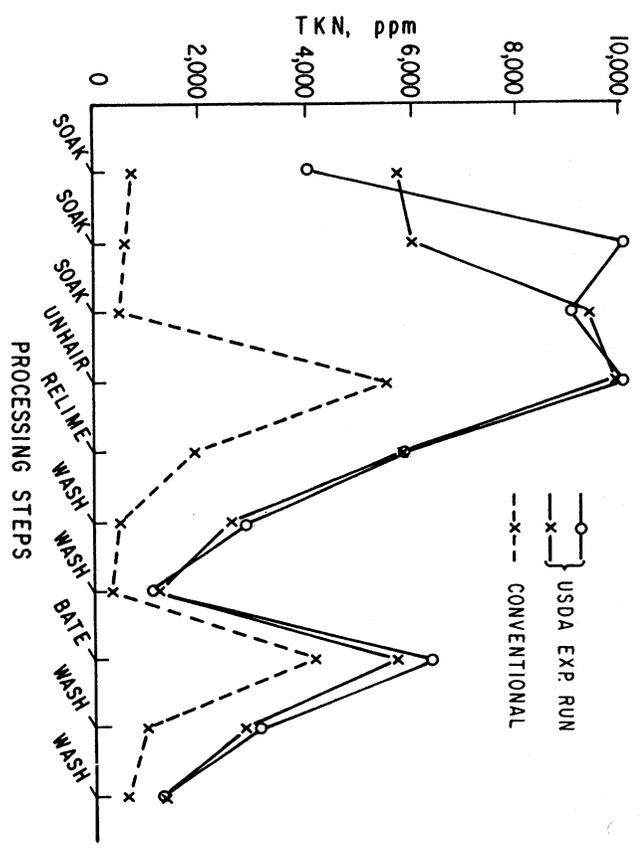


FIGURE 6. — Total Kjeldahl nitrogen content in effluent streams.

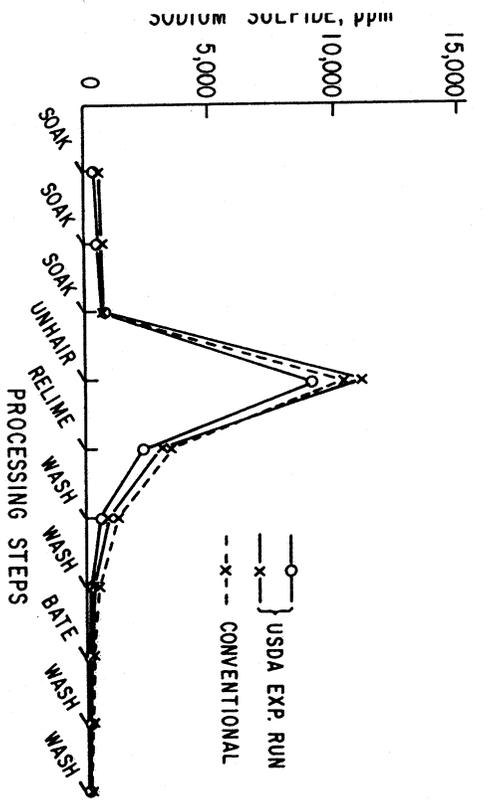


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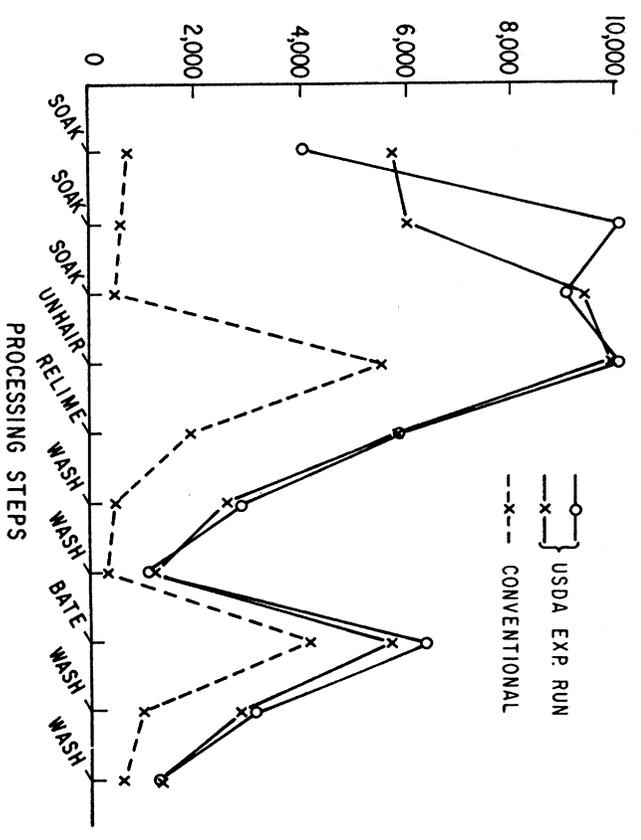


FIGURE 6. - Total Kjeldahl nitrogen content in effluent streams.

two peaks, one at bating and another at unhairing. The peak in the bate is practically identical with the ammonia curve in Figure 4. The unhairing peak is, of course, due to dissolution of hair. The TKN drop in post-relime wash 2 is due to ammonia evaporation or stripping, and in soak 3 to centrifugation of suspended solids. The centrifugation does not remove nitrogen as thoroughly as it removes calcium. Additional TKN is generated during soaking. Consequently, there is a progressive build-up of TKN when going from soak 3 to soak 1. In this respect, the countercurrent process differs from the conventional process. Observe, however, that the solid curves are close together indicating that the process is stable with respect to TKN and that approximately the same amount of TKN is present in any step from run to run.

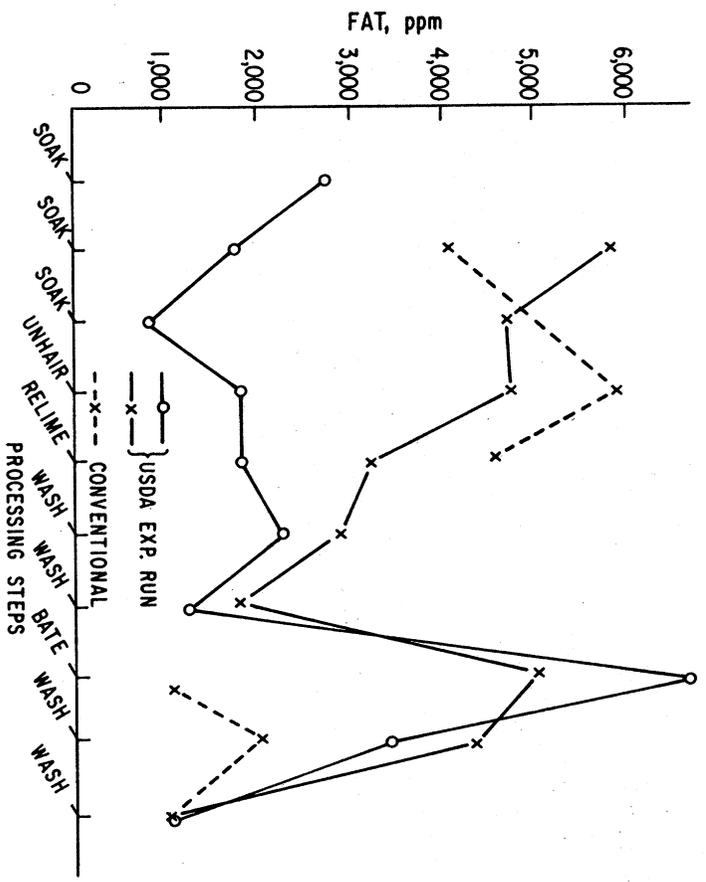


FIGURE 7. - Fat content in effluent streams.

The distribution of fat (Figure 7) in the effluents from the processing steps of the countercurrent process and the conventional process was also found to differ. In the countercurrent process, the bating solution had the highest amount of fat, while in the conventional process the fat was removed from the hide in the soak-

ing step. In brined hides, much of the fat is in the form of the sodium salt of the fatty acids, or soap. When contacted with fresh water during conventional soaking, part of the soap is washed out. This does not occur as readily when the hide is contacted with salt water because soap becomes less soluble as the ionic strength is increased. For example, in the manufacture of soap, 10 to 12 percent salt is added to precipitate the soap from the glycerine byproduct. As will be discussed shortly, this lack of fat removal may be responsible for a somewhat nonuniformly colored surface of chrome-tanned, dyed, and fatliquored leather produced by the countercurrent process.

While the two types of processes differ significantly, the conditions to which the hides are exposed differ little. It is not surprising, therefore, that the physical properties of leathers made by both processes are similar. The physical strength of wet blue stock produced by countercurrent water reuse is of the same order of magnitude as the strength of leather made conventionally using fresh water. This can be seen from Table II by comparing line 2, which gives data obtained in a conventional run using fresh water, with lines 3 to 6 which gives data for USDA runs O, P, Q, and R. As a matter of fact, by comparing line 1 with lines 3 to 6, it is seen that the tensile strength, the stitching tear, and the ball bursting strength of samples from the countercurrent effluent reuse process which were taken from the butt area, are similar also to leather made at ERRC using commercial processing schemes.

TABLE II

PHYSICAL PROPERTIES OF WRUNG BLUE STOCK			
Run #	Tensile lb/in	Stitch tear lb/in	Ball burst lb/in
Commercial	2741 - 6476	690 - 822	1850 - 2353
USDA fresh H ₂ O	3336 - 4412	829 - 932	922 - 1224
USDA Counter- current run			
O	2221 - 3356	776 - 914	1576 - 1926
P	3978 - 4337	810 - 895	2579 - 2584
Q	3323 - 3620	736 - 839	2050 - 2687
R	2584 - 5211	707 - 855	1633 - 2266

The leather produced by countercurrent processing is also similar in chemical composition to leathers made by conventional and by commercial processing, as can be seen from Table III.

The leather made by the countercurrent procedure did differ however, from the other two types of leather in visual appearance, being slightly less uniform in color when fatliquored and dyed light brown. The patches of slightly darker shade usually disappeared on extraction of samples of the dyed leather with acetone. It was assumed that fat or calcium soaps were not sufficiently removed from the

TABLE III
CHEMICAL ANALYSIS OF BLUE STOCK
 (Percent on moisture-free basis)

Analysis	Commercial (typical)		USDA fresh H ₂ O	USDA countercurrent	
				Run Q	Run R
Ash	9.62, 12.64	13.04	13.57	14.65	
Vol. Sol.	90.38, 83.36	86.96	86.43	85.35	
TKN					
(AF, FF)	16.70, 16.45	16.94	16.58	16.00	
Cl	0.9, 1.54	3.95	2.25	2.13	
Cr	2.36	2.24	2.05	2.05	
Na	—	3.31	2.81	2.27	
Ca	1.36, 0.61	0.1665	0.34	0.63	
S	—	1.89	2.07	2.18	
Fe (ppm)	—	398	155	152	
Fat (AF)	2.81	12.02	2.69	5.23	
Cr/S	—	1.18	0.99	0.94	

surface causing unevenness in uptake of the fatliquor and dye. Addition of 0.1 percent Triton X-114 in post-relime wash 2 and in post-bate wash 1 helped greatly, adding support for this assumption. The use of a drum instead of a hide processor eliminated the problem almost completely. This suggests that increased mechanical action helps to distribute fats and soaps more evenly in addition to helping in their removal from the hide. The effect of mechanical action on the visual appearance of the leather will be studied in the future. In addition, surface active agents will be added in the soak. If the problem is still not eliminated, addition of lime-soap dispersing agents to the soak and increased mechanical action will be utilized.

Based on the results obtained to date, it can be concluded that countercurrent reuse of process streams can yield stable processing conditions and uniform quality from run to run. With this systematic water reuse, approximately 90 percent of the fresh water conventionally required to process hides to the pickle stage can be saved. Leather obtainable by countercurrent reuse is found to be equal in physical properties and chemical composition to leather made by using fresh water in each operation. A less uniform uptake of dye during countercurrent processing appears to be surmountable by adding surface active agents and increasing mechanical action.

Acknowledgments

The authors thank Mr. Bohdan Artymyshyn, Mr. Edward DellaMonica, Mr. Edward J. Diefendorf, Miss Mary V. Hannigan, and Mrs. Paula Sweeny of ERRC for their invaluable help in evaluating the leathers.

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Received December 30, 1981

Discussion

MR. MARCEL SIEGLER (Seton Leather Co., Discussion Leader): Mike, I want to thank and congratulate you for your interesting and original approach to this subject. Of the many studies and research publications about effluents we have all read, I think this solution, presented by USDA, is one of the most practical, simple, and economical. It will interest many tanners. Being the moderator, I would like to take the privilege of asking the first question. Because we at Seton Leather use a lot of fresh hides, I would like to know if you ran some tests with fresh hides?

MR. KOMANOWSKY: No, we didn't. But we hope to.

MR. SIEGLER: Do you think there would be any problems in using this approach for fresh hides?

MR. KOMANOWSKY: I expect not. I am eager to try fresh hides because with fresh hides, I believe one wouldn't have the problems we encountered with brined hides. Salt would not be there to interfere with the removal of the calcium soap in the soaking step or of the epidermis during unhairing and reliming.

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Mr. SIEGLER: In this case Mike, what effect do you think the salt would have? In fresh hides we don't have any salt. I believe you mentioned in the paper that about 2.5 percent salt is ideal.

Mr. KOMANOWSKY: Well, in some of our studies we have looked at the effect of salt during different processing stages. We all know how the salt content in the soaking step affects removal of proteins. We also know that for opening up of the hide structure, we must not have too much salt in the hide. But in our work we found that the presence of salt affects the rate of unhairing; although this fact has not been clearly explained in the literature to date. And, interestingly, the unhairing rate manifests itself in a way similar to the swelling effect. At approximately 2 percent, the unhairing rate is the highest; at lower salt concentrations, the unhairing rate decreases somewhat, and at very high salt concentrations it is really, really low.

Mr. SIEGLER: Now I would like to turn to the floor.

Dr. STANLEY SHUTTLEWORTH (LIRI, Grahamstown, South Africa): I thought it might be interesting in this discussion to mention that some of our tanners in South Africa are recycling from their second or third ponds through the beam-house, not through the chrome section, and have been doing it for several years, with success, in spite of the salt buildup. I think that the little difference can be corrected easily with a small addition of sulfide. Those of you who have aerated ponds with straight chrome tanning could benefit considerably, because in many cases your effluent standards are related to the weight of the hide used.

Another system which is being actively encouraged by our authorities is the use of purified local authority waste. In our case, the local authority wastes have to be purified to full health and general standards before discharging into the rivers. They are very keen that tanners and other industries should utilize this water and this helps the tannery survive against activities of the authorities. In this case, we find that all processes in the tannery, except dyeing, can be successfully operated with purified city waste.

Mr. KOMANOWSKY: When using 100 percent float, we observed that much of the solution was absorbed into the brined hide; the salt concentration in the soak was higher than expected, and we had problems with unhairing. Instead of increasing the float, we increased the sulfide concentration, and we observed a decrease in leather quality. But there may have been other reasons for this. We have not done enough research to date to ascertain whether the decrease in hide quality resulted from the increase in sulfide ion concentration. However, as I mentioned before, I still feel strongly that one does have to have stable conditions. A tanner must accomplish satisfactory removal of hair in a definite length of time, or his schedule will be upset. A tanner must also have a consistent salt concentration in the relime if he expects to open up the structure of the hide to the same degree from run to run. So, I must disagree that a procedure with a variable salt content is as good as this countercurrent procedure.

DR. SHUTTLEWORTH: Two answers to that: First, you should have a talk with Bob Sayers — it is a pity that he is not here — who has processed a lot of green hides. We did an investigation, and I think this has been repeated in other countries, on the use of sea water which has over 3 percent salt and, there again, this can be utilized in the whole tannery except the dye bath with no problems.

MR. KOMANOWSKY: Unfortunately, if you continue reusing sea water when processing brined hides, the salt concentration will increase beyond 4 percent. And with a steadily rising salt concentration you won't have the stable conditions necessary to ensure consistently good leather quality.

MR. SATYENDRA DE (W. D. Byron and Sons, Inc.): I have one question. How long did your experimental method take to eliminate the ammonia completely from your exhaust bate liquor?

MR. KOMANOWSKY: Actually, we are still in the process of installing the equipment for stripping the ammonia and reabsorbing it in acid solutions. At the present time, we simply boil it off before we reuse the bating solution.

MR. DE: Ammonia removal by air stripping may take a comparatively long time and so it could be a stricture in your whole process.

MR. KOMANOWSKY: No. Before we purchased the equipment, I made calculations using data available in the literature. According to the calculations, it should be possible to pass the concentrated bating solution through a packed column and to remove most of the ammonia in a fairly short time.

MR. SIEGLER: I am sorry that our time is up and I must close this interesting discussion. Thank you, again, Mike, for this fine presentation.