RECENT DEVELOPMENTS IN TANNERY PROCESS MODIFICATION FOR REDUCING LIQUID AND SOLID WASTES*

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INTRODUCTION

A paper on no-effluent tanning processes by Williams-Wynn was read at this convention four years ago. Since that time considerable progress has been made by leather chemists in tannery process modification to eliminate intractables in the effluent, and many tanneries are using these modifications successfully with considerable savings in materials, as well as making a major contribution to the effluent problem.

WATER USAGE

Traditionally tanneries were established near rivers, from which water was extracted free of charge, and mostly in unlimited supply. Countries such as South Africa have had to conserve water to an increasing extent, and much attention has been paid to water economy. Changing from continuous to batch washing has been a major factor. Other steps have included liming in second soak waters, chrome tanning in pickle liquors, and using reduced floats with drums and mixers and more concentrated liquors generally.

A recent successful development in South Africa has been the recycling of water from effluent ponds for use in the beamhouse. Two major South African tanneries are using this system and others are preparing to follow. A 30 percent economy in water is achieved, plus an equivalent reduction in evaporation pond area required, which has enabled these tanneries to expand their production without additional water or pond area. In an evaporation pond system the water is recycled from the middle of the series as the final ponds are more saline.

Whereas the normal tannery water usage is stated (1) to be 50 liters per kg. of hide, South African tanners are down to 11.25 liters per kg. One problem of water economy is that the effluent analyses are proportionately worse. This aggravates the acceptance problem where local authorities set limits based on analyses rather than on total content.

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SALTS

The need to eliminate dissolved salts from tannery effluent varies widely. In countries like the U.S.A., with vast rivers and estuaries, the authorities have not yet set ceilings for total dissolved solids. However, Maine and Sundgren (2) have stressed the desirability of using salt-free hides where effluent disposal is by irrigation of land. In South Africa, the TDS ceiling of 1000 p.p.m. is impossbly strict where tanners purchase salt-cured hides. However, as pointed out in a recent paper from the U. S. Eastern Regional Research Center (3), the desirability of eliminating the use of salt in curing is already being anticipated by work on comparisons between uncured and salt-cured hides in tanning. Although a good deal of processing of fresh hides from the slaughter house or abattoir is already taking place in many parts of the world, the majority of tanneries are not situated sufficiently close to this source to take advantage of it. Furthermore the regular daily availability of the correct hide weights and types does not generally match the tanners' requirements. The production of wet blue and crust vegetable using uncured hides from freshly slaughtered animals is one solution to this salt elimination problem. Another solution is the use of alternative curing methods and much progress has been made in this direction (4–7). In South Africa two types of cure are envisaged. One of these is a short cure of seven to ten days to enable hides to be carted by road transportation and to be sorted and stored at the tannery. The other is a longer cure aimed at more distant markets. Such hides would have to be purchased on green weight, as variations in moisture content would provide too great an area of dispute, salt curing having the virtue of a reasonably stable product in terms of yield.

LIME

Lime has provided tanners with a low cost, well buffered alkali for unhairing, and it has been traditional to use it in excess. This has been desirable in non-agitated pit systems, where a coating of lime on the hides offsets the problem of low solubility. However, with the use of drums and mixers, this coating is no longer needed. Lime in the effluent buffers the high pH of beamhouse liquors against neutralization and is an intractable constituent of solid waste.

Much work is being carried out on lime-free unhairing systems (8–11), but I do not propose to overlap with Peter van Vlimmeren's paper at this convention.

Work carried out at L.I.R.I. on both chrome- and vegetable-tanned leather (12–15) indicates that lime levels can be reduced to as low as 0.5 percent without the use of caustic soda, using either sulfide or sulfhydrate as sharpening agent. The use of caustic soda instead of lime is also feasible for upper leather and is in fact extensively used in England for gloving leather. L.I.R.I. work (16) suggests that not more than one percent should be used and that sodium sulfhydrate is the best sharpening agent.

. Most South African tanners have reduced their lime level to two percent on soaked weight, and the result is that a surface aerator used on the beamhouse effluent will eliminate sulfide and drop the pH below 9.0 in a few hours without complaint by the neighbors, with substantial reduction in solid wastes.

A statistical evaluation of the effects of lime reduction on the physical and aesthetic properties of chrome-tanned side leather (17) has indicated that this reduction can be balanced by choice and level of sharpening agent. Of the physical tests applied in this experiment the lastometer extension in mm. gave the best indication of property variables, the other physical tests showing little or no significant differences. Tables I to IV show these results.

TABLE I

Level of Sharpening Agent Addition	Level of Lime Addition				Mean
	2.0%	2.5%	1.0%	0.5%	
3.0%	13.25	14.35	11.90	11.20	12.68
2.5%	13.15	11.0	11.35	12.80	12.08
2.0%	13.10	12.20	11.70	12.30	12.33
1.5%	12.85	14.75	13.00	12.80	13.35
Mean	13.09	13.08	11.99	12.28	12.61

TABLE II

Type of Sharpening Agent	Lime Addition		Mean
	2.0%	1.0%	
Sulfide	13.26	11.60	12.43
Sulfhydrate	12.9	12.66	12.78
Mean	13.08	12.13	12.61

TABLE III

Type of Sharpening Agent	Level of Addition of S/A		Mean
	3.0%	2.5%	
Sulfide	11.53	13.34	12.44
Sulfhydrate	13.48	12.08	12.78
Mean	12.51	12.71	12.61

TABLE IV

Float Length	Level of S/A Addition		Mean
	3.0%	2.5%	
50%	12.93	12.26	12.61
75%	12.06	13.16	12.61
Mean	12.51	12.71	12.61

The normal acceptance level for a footwear factory is 8 mm., and all samples passed this, the averages being well above this limit. Examination of aesthetic properties did not reveal any guidelines.

Spent lime liquor from a low lime system may be eliminated altogether by being used up in the second soak of a double soak system, the first soak being to wash out the surplus salt and break open the pack (17). The spent sulfide or sulfhydrate plus spent lime act as soak accelerators. The system is illustrated in Figure 1.

FIGURE 1

Schematic Illustration of Liquor Flow

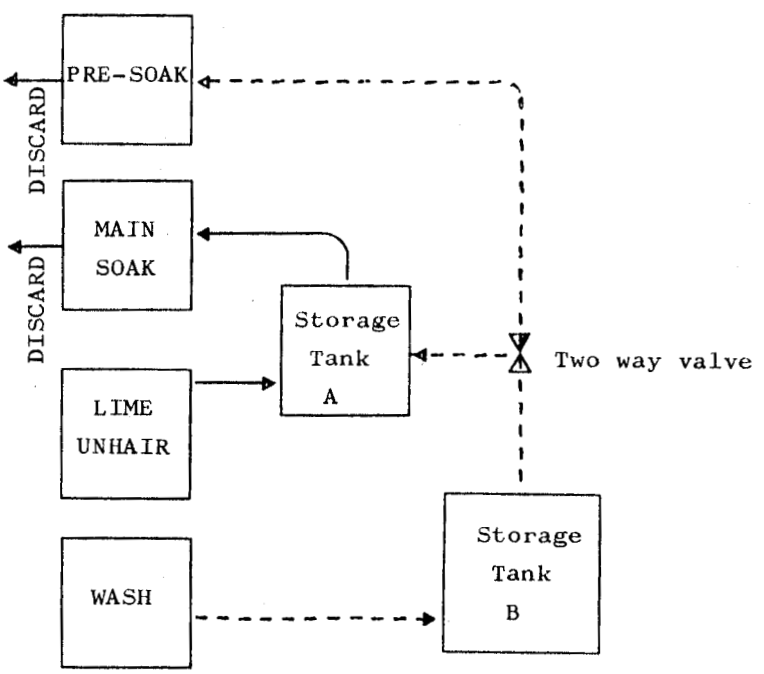

Table V shows the analytical results from a two percent lime-3 percent sodium sulfide unhairing system. The table clearly indicates that, by using a system such as the one proposed, it is quite possible to remove all lime from the beamhouse effluent before that effluent reaches the treatment plant. A statistical evaluation of the leathers produced showed no significant effects on the physical test results or aesthetic properties.

TABLE V

Liquor Description	g. $Ca(OH_2)$/liter	
	After Unhairing	Final Effluent
Spent Liquor (U/L) cycle 1	0.139	
Wash water cycle 1	0.032	
W/water cycle 1 as pre-soak cycle 2		0.0
U/L mixed with W/W, soak cycle 2		0.0
Spent Liquor (U/L) cycle 2	0.139	
W/water cycle 2	0.051	
W/water cycle 2 as pre-soak cycle 3		0.0
U/L mixed with W/W, soak cycle 3		0.0
Spent liquor (U/L) cycle 3	0.111	
W/water cycle 3	0.043	
W/water cycle 3 as pre-soak cycle 4		0.0
U/L mixed with W/W, soak cycle 4		0.0
Spent Liquor (U/L) cycle 4	0.131	
W/water cycle 4	0.037	
W/water cycle 4 as pre-soak cycle 5		0.0
U/L mixed with W/W, soak cycle 5		0.0
Spent Liquor cycle 5	0.134	
W/water cycle 5	0.064	
W/water cycle 5 as pre-soak cycle 6		0.0
U/L mixed with W/W, soak cycle 6		0.0
Spent Liquor cycle 6	0.148	
W/water cycle 6	0.028	

The following code has been used:
U/L = Unhairing lime liquor.
W/W or W/water = lime wash water.

Another possibility is the recycling of beamhouse liquors. Money and Adminis (18) have shown that lime sulfide liquors can be recycled more than 20 times on pilot-plant scale without apparent loss of quality in the resulting leather. One of the larger South African side leather manufacturers is at present adopting a lime recycling method and hopes to achieve economies in lime and sulfide usage, as well as assisting the effluent problem.

CHROME

Although it can be established that spent chrome tannery liquors are not as toxic as the prevailing acceptance standards suggest, it is difficult to achieve a relaxation of these standards. Precipitation of the chromium by blending with the beamhouse liquors merely transfers the problem from the liquid to the solid effluent.

Recovery of chromium from spent chrome liquors has been investigated by Harnley (19) and Hauck (20) and has been in large scale practice in many countries. Some forty years ago the writer visited a tannery at Leeds, England, where the spent chrome liquor was treated with sodium carbonate and the precipitated chromium hydroxide compacted by centrifuge, redissolved, and reused.

In recent years methods of recycling in the tan yard have been studied by Miller (21) and Davis and Scroggie (22). We have checked this work in pilot plant and factory trials, and about half of our South African tanneries are now using chrome recycling for reasons of economy to offset the increased cost of chrome tanning salts.

There are two methods used in practice. The simplest method, requiring very little control, is to reuse the spent chrome as the pickle. The main precaution is that the pickle acid should be added to the spent chrome liquor before running into the drum from the storage tank. Otherwise the basic liquor will overtan the grain.

Many modern tanneries, however, add the chromium salts in powder form to the drum at the end of the pickling operation. In this case the spent chrome is pumped out to the storage tank, acidified, and then used as the next pickle. The acid could be either sulfuric or formic, and the problem is whether changes in liquor character will result in changes in leather quality. This has been studied (23) in the L.I.R.I. pilot plant. Table VI shows the analytical data of the spent chrome tanning liquors for either sulfuric or formic acids. No salt was added, apart from that carried over with the hide pieces. The sodium formate added for Treatment A was ten percent of the weight of the chrome tanning powder added. The latter was calculated to give a total, with the spent chrome, of eight percent of the limed hide weight.

It is evident that the sulfate content of the spent chrome tanning liquors rapidly reached equilibrium and was fairly constant after four cycles. The higher sulfate concentration of Treatment A is due to higher sulfuric acid plus formate masking. The chloride content of the spent liquors decreased from 1.8 percent for run 1 to 0.08 percent for run 6 for both treatments, but this was compensated for by the increased sulfate contents and chemical analysis and physical tests showed no trends or deficiencies.

The method requires regular spent chrome analyses at the start and periodic

TABLE VI

ANALYTICAL DATA OF SPENT CHROME-TANNING LIQUORS

Run	Treatment A (1% H_2SO_4 + Sodium Formate)		Treatment B (0.8% H_2SO_4 Only)	
	Cr_2O_3%	SO_4%	Cr_2O_3%	SO_4%
1	0.76	1.84	0.65	1.74
2	0.74	2.41	0.62	2.30
3	0.71	2.88	0.52	2.61
4	0.72	3.38	0.44	2.82
5	0.72	3.59	0.47	2.75
6	0.74	3.67	0.51	3.23
7	0.70	3.73	0.45	2.91
8	0.74	3.67	0.62	3.03
9	0.70	3.81	0.65	2.92
10	0.68	3.67	0.59	2.85
11	0.72	3.84	0.55	3.02
12	0.74	3.91	0.51	3.16
13	0.70	3.81	0.55	2.98
14			0.57	3.08

checks subsequently. Screening of flesh and other particles removed by drumming would also be needed.

VEGETABLE TANS

The Tanning Extract Producers Federation survey of modern vegetable tannage (24) describes a number of processes where a minimum of vegetable tannins is discarded. Of these methods the only one which takes care of the considerable amount of tannin discarded in wash and bleach liquors appears to be the Liritan system (25). This also has the advantage of retaining the quality characteristics of an all-pit method, regarded by many as essential to the retention of the quality market for vegetable leather. Methods where the tannin is drummed into the leather in spray-dried form involve protection of the grain and this may be accomplished by prechroming, Calgon treatment, treatment with syntans, or the use of sodium sulfate, which is subsequently washed out to fix the tans. These processes are facilitated by the modern availability of spray-dried extracts.

Most tanners are adopting methods aimed at reducing vegetable tans in the effluent, as these are high in oxygen demand. When mixed with beamhouse liquors, a bulky sludge results, while any iron present produces a black ink. No effluent processes eliminate these problems.

RETANNING

Work at L.I.R.I. has shown (26, 27) that dry or low-float retanning gives a stronger leather, particularly where vegetable tannins are used, as there is more filling action and less crosslinking. Crosslinking gives a more rigid structure, with reduced grain elasticity and lower breaking strength. These dry or very low float retannages are more economical and avoid aggravation of the effluent problem.

DYEING

Work on cold leather dyeing processes without float has been carried out by Rosenbusch and Munch (28). More recently L.I.R.I. has been experimenting with a foam dyeing process, and successful large scale trials have been carried out. The method has not yet been adopted on the large scale. Little or no effluent results from the method, as the dye is taken up completely. A great deal of modern upper leather is not drum-dyed before finishing and this assists the effluent color problem.

GENERAL CONCLUSIONS

It is apparent that great strides have been made in eliminating the intractables from the liquid and solid effluents of the modern tannery, and many tanners are enthusiastic about these developments, not only because of the reduction in effluent problems, but also because of the economics involved. It is possible to envisage the tannery of the future using unsalted hides and producing mainly proteinaceous effluent which can be utilized as food for pigs or chickens or as fertilizer.

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DISCUSSION

MR. L. K. BARBER (A. C. Lawrence Leather Company): Thank you very much, Stanley. I think that Stanley has given us an especially valuable overview of his assessment of trends in the tanning world today from a very practical point of view. This paper is certainly worthy of detailed study.

One especially interesting point is the use of lime as many as twenty times. When you reuse something as many as twenty times that begins to suggest permanency of reuse. Perhaps it is possible to reuse rather than sewering our lime liquors with the resultant problems in coping with the lime solids in the effluent.

We have not gone far enough to really prove it out, but at one of our sole leather tanneries we started about four months ago to stop sewering lime solids from our hair-saving reel-over system. We are not sewering any lime solids from three of our six lime rows at that tannery. So far we can not detect any difference in the appearance, feel, plumpness, and other properties of the hides coming out of lime. They unhair equally well, perhaps a little better. This approach looks especially promising because it saves money instead of spending it in waste water handling. Are there questions from the floor?

DR. SHUTTLEWORTH: We questioned the French about their work. Their conclusion was that, in view of consistency since the eighth re-use, they could regard it as a permanent solution, with lime sewering never being necessary.

MR. S. S. SARYAN (Wolverine World Wide, Inc.): Dr. Shuttleworth, do you expect any difficulties on the reuse of chrome many times on the production of suede leather *versus* side upper leather?

DR. SHUTTLEWORTH: Our tanners make a wide variety of leathers in a single tannery. They don't observe any difficulties with a wide variety of leathers.

MR. SARYAN: Do you expect any unlevelness in suede leather?

DR. SHUTTLEWORTH: No, I do not think so. Use of the chrome in the pickle won't cause any problems. The main requirement in making suede leather is to get firm fibers which "stand" up for buffing. In chrome recycling you simply restore the chrome to the normal levels. We produce a lot of suede without coloring problems.

MR. SIGMUND PANZER (Robson-Lang Leathers Ltd.): Would you please expand on foam dyeing?

DR. SHUTTLEWORTH: We are not yet ready to publish this. However, it has been found in the textile industry that a level shade can be secured with practically no float by carrying the dye on the surface of a foam. This works very well. However, for use on a commercial scale you must know that it works with all the dyes that are used. We want to evaluate the process with all the dyestuffs used in South Africa. We have already used it on simple types of black and brown leathers without problems in full scale runs. Of course, drum dyeing is used less today. People are now coloring with a spray gun which will reduce dye in the effluent.

DR. ROSS G. DONOVAN (Canada Packers Ltd.): I am sorry that time requires us to terminate this discussion. Thank you, Dr. Shuttleworth.

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