

Recycling comes to tanning

Tanning hides to produce leather has traditionally been a messy process. The hides are soaked in a series of liquors, and when these have done their work they contain pollutants including:

- ▶ degraded proteins, which have a large appetite for the oxygen dissolved in water
- ▶ chromium, a toxic heavy metal
- ▶ sodium sulphide, which can react with acids to produce dangerous, foul-smelling, hydrogen sulphide gas

Effluent disposal has become a major problem for tanneries in recent years with the introduction and tightening of controls on what can be discharged into sewers. Normally solids such as hide pieces, flesh, and fat are removed by screening. Then the effluents from different processes are mixed in a way that encourages things such as chromium, tannins, dyestuffs, and proteins to precipitate. The precipitated material is separated, with varying degrees of completeness, and collected as a sludge that is dumped on land. The remaining liquid goes into the sewers.

A tannery handling 500 hides a day is likely to produce more than 2 million litres of liquid effluent a week, and it is estimated that the total annual output of liquid effluent from Australia's tanneries is about 1800 million litres.

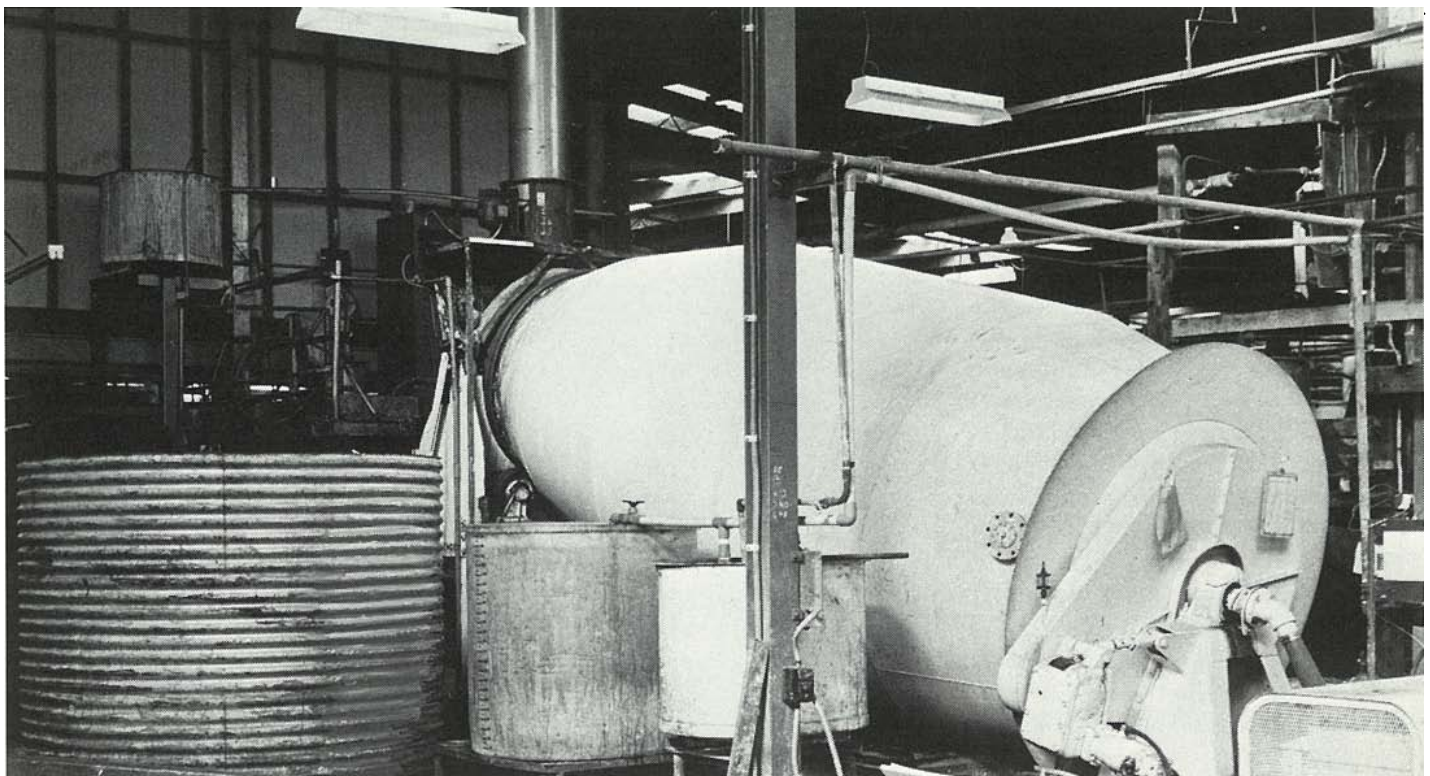
Sludge production from a relatively large plant can approach 50 000 litres a week. Research by Dr Jim Scroggie and his colleagues in the Leather Research Group of the CSIRO Division of Protein Chemistry in Melbourne has now shown how effluent production can be greatly reduced, and discharge of the worst pollutants virtually eliminated.

The hides are unhaired

When cattle hides come into a tannery, their hair has to be removed. The main chemicals in the liquor that does this job are lime and sodium sulphide. Present practice is to discard the liquor after each batch of hides has been unhaired, and it is estimated that this is the source of about 85% of the pollutants in tannery effluent. Degraded proteins from the removed hair, sodium sulphide, and lime are the main pollutants from this process.

For many years research has been going on in Australia and overseas into ways to use enzymes in place of lime and sodium sulphide for the unhairing job. Unlike the sulphide process, the enzyme process doesn't destroy the hair, so degraded protein is largely excluded from the effluent. Also, as there is no sodium sulphide in the effluent, there is no risk of producing hydrogen sulphide gas. The research looked promising for a long time, and the Leather Research Group and researchers overseas are continuing with it. However,

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Inside a tannery—the hide-processor used in a recycling trial.

it hasn't yet proved possible to consistently produce the soft and flexible leather that the market demands from hides unhaird by the enzyme process, and sometimes enzymes don't completely remove the hair.

Two years ago Dr Scroggie's group decided to see if recycling could ease the effluent problem. The answer has turned out to be a resounding yes. Research by Mrs Catherine Money has shown that the lime-sulphide unhairing liquors used by all Australian tanneries can be recycled more than 20 times and possibly indefinitely. The cost to tanneries of switching over to recycling should in most cases be small; the main expense, unless extra space has to be created for the new plumbing, will be for a storage tank for the used mixture. This should cost, on average, about \$2000.

Between uses, the liquor has to be reconstituted with lime, sodium sulphide, and water. However, because unused lime and sulphide are not discharged in the effluent, there is a reduction in the amounts of these used and hence some cost saving. Solids that accumulate in the mixture have to be removed after every few uses, and outlets for these are being sought.

No change in quality

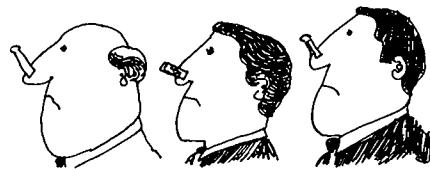
Mrs Money has detected no change in leather quality or yield produced by re-

cycled lime liquors. If tanneries recycle indefinitely, liquid effluent from this part of the tanning process will be virtually eliminated. If they discard the mixture after, say, 20 uses, they should achieve an aggregate 20-fold reduction in the amount of sulphide discharged in the effluent and about a 10-fold reduction in the protein output.

The process that puts chromium into the effluent is chrome-tanning. When the liquor used for this is thrown out after one use—the normal practice—about a quarter of the chromium sulphate used for tanning is lost in the effluent. Mrs Margaret Davis and Dr Scroggie have found that this liquor can be re-used indefinitely if it is reconstituted with chromium sulphate after each use and solids are removed after every few uses. As chromium is fairly expensive, the saving in reagent costs here is considerable; the scientists have estimated that if the entire hide-tanning industry in Australia adopted recycling in chrome-tanning it would save about \$250 000 a year.

The plumbing needed is similar to that needed for lime-sulphide recycling, and should cost about the same. Recycling almost completely eliminates chromium from tannery effluent, and again trials have shown that there is no adverse effect on leather quality.

Both these recycling processes have been tried successfully in tanneries. The



chrome process, the first to be proved, is now in regular operation in some tanneries and others are introducing it. Some tanning companies have also announced that they will adopt the lime-sulphide process.

Uses for sludge

The sludge that tanneries produce contains a considerable amount of protein. If the sludge can be kept largely free of chromium, as it is when the chrome-tanning mixture is recycled, it may be possible to put it to good use as stock feed or fertilizer. Dr Scroggie's group has recently begun investigating possible uses in the hope of removing the need to dump the sludge, and the prospects seem bright. Stock feed is probably the most economically attractive use at present, and research is under way to work out the best ways to incorporate the sludge into commercial stock feed. A manufacturer has conducted production trials with encouraging results.

The Leather Industry Research Association, an industry body representing 26 tanning companies, is helping pay for the research. Tanning is an important industry in Australia; it produces leather worth about \$80m each year. Soon it should be a much cleaner industry.

More about the topic

Investigation of commercial chrome-tanning systems. I. Separation of the complexes present by gel filtration and the effects of ageing and basification. II. The rate of uptake by hide of the different chromium complexes from solution. III. Re-cycling of used chrome liquors. IV. Re-cycling of chrome liquors and their use as a basis for pickling. V. Recycling of chrome liquors in commercial practice. M. H. Davis and J. G. Scroggie. *Journal of the Society of Leather Technologists and Chemists*, 1973, **57**, 13-18; 35-8; 53-8; 81-3; and 173-6.

Recycling of lime-sulphide unhairing liquors. I. Small-scale trials. C. A. Money and V. Adminis. *Journal of the Society of Leather Technologists and Chemists*, 1974, **58** (in press).



Mrs Money at work.