THE RECYCLING OF CHROME TANNING LIQUORS

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Manchester, N. H. 03101

AND

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ABSTRACT

In order to decrease the amount of chromium discharged into the tannery effluent, a recycling system was developed. The system is based on the pumping of the spent chromium solution from hide processors through a screening system and into a storage tank for equalization. The equalized chrome liquor is used as the pickle liquor. Data are given on the tanning processes, including material balances and material costs.

INTRODUCTION

The recycling of chrome tanning liquors is not new. During the days of paddle tannage, it was common practice for tanners to keep the chrome tanning bath (1). Either pickled or bated hides would go through the chrome tanning cycle in approximately 24 to 48 hours. The chrome-tanned leather would be pulled, and the spent solutions analyzed for chrome, salt, and basicity. Additional salt, acid, and chrome tanning salts would be added and the bated stock would be introduced into the tannage.

Under this system, the saving of chrome was considerable. Spent solution of chrome tanning may contain as much as half of the chromium or tanning agent that was used in the original tannage. After the tannage was used from four to six times, the spent chrome liquor could be used for retanning of splits or dumped. The dumping of the chrome tanning liquor was to prevent the build-

*The systems described in this paper were the results of developments made in 1972. Since that time the company has changed its chrome tanning system and is now recycling chrome liquor from drums in a bate, pickle, and tan system. The chrome tanning wastes by either approach result in essentially zero chromium discharge.

**Present address: W. D. Byron Co., Williamsport, Md.
up of sodium sulfate and other material in the chrome tanning bath. With the passing of chrome tanning from the paddle tannage to drums and hide processors, the concept of recycling of chrome liquors was discarded.

There is now renewed interest in this approach with the need to decrease the chromium being discharged in the effluent (2). Several possible methods are available to the tanner. The pH of the effluent may be raised to above the precipitation point of the chromium, and the chrome salts removed by settling. It has been suggested by several workers that the chrome tanning solutions can be precipitated separately. The hydrated chrome oxide precipitate can then be redissolved in acid, and the chrome tanning salt reused. This method requires specialized equipment and handling of the materials.

In the case of Seal Tanning Company, the Environmental Protection Agency asked the company to decrease the chromium being discharged into the Merrimack River. At the time the company was tanning in tanning drums, using a conventional bating, pickling, and tan process. The spent chrome liquor was being dumped on to the floor, through the floor drains, and into the river. It was imperative that a solution to the chrome discharge be found as quickly as possible.

The present report covers only the development of the chrome tan recycling system. The remainder of the wastes are being dumped, untreated, into the river. More extensive pretreatment will be required on the tannery effluent in the near future. At present, the company and this laboratory are determining the feasibility of several possible pretreatment and complete treatment plans.

**Theory of Chrome Recycling.** In the paddle tannage system of chrome tanning and recycling, the most common method was to introduce the bated stock into the spent chrome tanning bath, which was used as a pickle solution. The spent chrome liquor, with a pH of 3½ to 4, was refortified with salt and acid to drop the pH to less than 2, before the introduction of the bated stock. The bated hides would then be run in the pickle solution containing approximately 1/3 of the total amount of chrome needed for tannage. After a period of time, the remaining chrome tanning material was introduced. The tan proceeded for approximately 24 hours, after which the basification took place and the tan continued through the following day. This resulted in approximately a 48-hour process.

There was a certain build-up of salts in the spent chrome liquor as it was recycled, and this was a function of the liquor ratios used during the tannage. The total amount of water brought in with the bated stock and the total amount of water lost with the pulling of the chrome tanned sides was approximately equal. As more chrome tanning salts were added, there was a dilution effect, due to the addition of water from the bated stock. The build-up of salts did not proceed as a strictly linear function, but rather has a tendency to level off after a number of times of reuse.
In the case of the drum tannage, a different technique must be used. The spent chrome liquor removed from the drum can be stored in a tank and then introduced back into the drum with added salt and acid as part of the pickle solution. In this case the dilution effect from the bathed stock is more pronounced, and the build-up of materials becomes considerably less. The quantity of inert salt build-up can be calculated from the formula shown in Table I.

**TABLE I**

**BUILD-UP OF INERT SALTS**

<table>
<thead>
<tr>
<th>Concentration of SO₄ in Spent Solution</th>
<th>SO₄ from Stock + SO₄ in Spent Liquor</th>
<th>Volume of Stock + Spent Liquor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**THUS: At 3% SO₄ used**

<table>
<thead>
<tr>
<th>Percent SO₄*</th>
<th>At the End of Run No.</th>
<th>@ 3:1 Liquor Ratio</th>
<th>@ 1:1 Liquor Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>0.75%</td>
<td>1.5%</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.31%</td>
<td>2.25%</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1.74%</td>
<td>2.62%</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>2.04%</td>
<td>2.8%</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>2.28%</td>
<td>2.9%</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>2.46%</td>
<td>2.95%</td>
</tr>
</tbody>
</table>

*Calculated from above formula.

The problem of mechanically handling the spent liquors from drums is much more complicated than the handling of the spent liquors in paddle tannages. The problem of liquor handling is greatly simplified by the use of a hide processor. A recycling pump is part of the regular equipment. Thus, to remove the spent liquor from the tannage, the spent liquor may be pumped directly to any tank or piping system as desired.

**The Seal Tanning System.** The spent liquor is pumped directly from the hide processors through a Hydrasieve, to remove suspended hide particles. After going through the Hydrasieve, the liquor is pumped to a storage tank. The storage tanks have sufficient volume to hold the discharge from six tannages. To remake the chrome solution, the spent chrome liquor is used for the pickle make-up solution as indicated in the formula (Table II and Table III).

There is a skim or overflow provided on the storage tanks to permit drawing off the accumulated grease to be discharged to the sewer. The grease may be removed without discharging significant quantities of chromium tanning salts.

Not all of the chromium can be recycled since there is more spent liquor discharged than is used in the pickle. When the amount of excess chrome liquor
TABLE II
HIDE PROCESSOR

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>WEIGHT:</td>
<td>24,000 lbs.</td>
</tr>
<tr>
<td>LOAD STOCK</td>
<td>Wash 10 minutes @ 75° and 20 minutes at 95°F.</td>
</tr>
<tr>
<td></td>
<td>Drain to cover stock.</td>
</tr>
<tr>
<td></td>
<td>ADD: 240 lbs. ammonium sulfate</td>
</tr>
<tr>
<td></td>
<td>24 lbs. bating enzyme.</td>
</tr>
<tr>
<td></td>
<td>Drain and wash 30 minutes @ 75°F.</td>
</tr>
<tr>
<td>DRAIN</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ADD: 800 gals. spent chrome</td>
</tr>
<tr>
<td></td>
<td>12 bags (1200 lbs.) salt — Run 15 minutes.</td>
</tr>
<tr>
<td></td>
<td>360 lbs. sulfuric acid — Run 2 hours.</td>
</tr>
<tr>
<td></td>
<td>Turn steam last ½ hour. Bring temperature up to 87°F.</td>
</tr>
<tr>
<td></td>
<td>Take liquor sample.</td>
</tr>
<tr>
<td></td>
<td>ADD: 240 lbs. calcium formate</td>
</tr>
<tr>
<td></td>
<td>290 gals. Tekchrome 42-A — Run 3 hours.</td>
</tr>
<tr>
<td>NEXT A.M.</td>
<td>Start mixer.</td>
</tr>
<tr>
<td></td>
<td>ADD: 260 lbs. bicarbonate @ 90°F. 2 Feeds. 30 minutes — Run 1 hour.</td>
</tr>
<tr>
<td></td>
<td>250 gallons.</td>
</tr>
</tbody>
</table>

TABLE III
REGULAR PROCEDURE

<table>
<thead>
<tr>
<th>Formulation:</th>
<th>BATE, PICKLE, AND TAN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basis:</td>
<td>12,000 lbs. lime trimmed stock</td>
</tr>
<tr>
<td>Drum:</td>
<td>10 x 10 16 R.P.M.</td>
</tr>
<tr>
<td>Wash 10 minutes @ 75° and 20 minutes @ 95°F.</td>
<td>Drain to 6&quot; to 8&quot; below gudgeon.</td>
</tr>
<tr>
<td>ADD:</td>
<td>0.1% (12 lbs.) bating enzyme</td>
</tr>
<tr>
<td></td>
<td>1% (120 lbs.) ammonium sulfate</td>
</tr>
<tr>
<td></td>
<td>Run 5. Stop 15 minutes.</td>
</tr>
<tr>
<td></td>
<td>Run 5. Stop 15 minutes.</td>
</tr>
<tr>
<td></td>
<td>Run 5 minutes.</td>
</tr>
<tr>
<td>Wash 30 minutes @ 75°F. Drain to 8&quot; below gudgeon.</td>
<td></td>
</tr>
<tr>
<td>ADD:</td>
<td>7.5% (900 lbs.) salt. Run 15 minutes.</td>
</tr>
<tr>
<td></td>
<td>1.5% (180 lbs.) sulfuric acid (dilute to cool). 150 gal.</td>
</tr>
<tr>
<td></td>
<td>Run 2 hours.</td>
</tr>
<tr>
<td>ADD:</td>
<td>1% (120 lbs.) calcium formate</td>
</tr>
<tr>
<td></td>
<td>Run ½ hour. Drain to 14&quot; below gudgeon.</td>
</tr>
<tr>
<td>ADD:</td>
<td>145 gals. commercial chrome liquor*</td>
</tr>
<tr>
<td></td>
<td>Run 3 hours.</td>
</tr>
<tr>
<td>NEXT A.M.</td>
<td></td>
</tr>
<tr>
<td>ADD:</td>
<td>180 lbs. bicarbonate @ 90°F. 2 Feeds 30 minutes</td>
</tr>
<tr>
<td></td>
<td>130 gal. Run 1 hour.</td>
</tr>
</tbody>
</table>

*1.421 lbs. Cr₂O₃/gal. 38% basic
reaches nearly a tankful, the following procedure is followed:

1. The grease is skimmed off.
2. The pH is raised to 10.0 with soda ash and sodium hydroxide.
3. The precipitated chromium hydroxide is settled.
4. The supernatant liquid is drawn off and discharged.
5. The chromium hydroxide sludge is dissolved in sulfuric acid and added to the spent liquor for recycling.

The presence of chrome tanning salts during the pickling operation did not cause any difficulty or significant variation in the quality of the leather or the stratigraphic distribution of the chrome during the tannage. The practical experience from paddle tannages would indicate that the method can be used with little difficulty.

The work of Thorstensen and Osugi (3, 4) on the penetration of pickled acids and chrome in the simultaneous chrome tanning/pickling operation has shown that the fixation of the chrome is a function of the pH in the stock. The chrome will penetrate following the pickle acid in accordance with the limits of pH of the system.

The saving in chrome would amount to approximately 19 gallons per batch; based on a price of 80¢ per gallon this is $15 for chrome tanning salt (Tables IV and V).

The savings in sodium chloride is 600 pounds of salt per 24,000 pounds of limed weight. At 2¢ per pound (delivered to the tannery) the savings are $12 per batch. The total savings then would be $15 plus $12, or $27 per 24,000 pounds of limed weight. The daily saving would then be approximately $108 per day (based on 4 batches per day) or about $30,000 per year.

**TABLE IV**

MATERIALS USED 24,000 LBS. LIMED STOCK

<table>
<thead>
<tr>
<th></th>
<th>Hide Processor</th>
<th>Two Drums</th>
<th>Hide Processor Saving Chrome</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium sulfate</td>
<td>240 lbs.</td>
<td>240 lbs.</td>
<td>240 lbs.</td>
</tr>
<tr>
<td>Bating enzyme</td>
<td>24 lbs.</td>
<td>24 lbs.</td>
<td>24 lbs.</td>
</tr>
<tr>
<td>Spent chrome liquor</td>
<td>800 gal.</td>
<td></td>
<td>24 lbs. Cr₂O₃</td>
</tr>
<tr>
<td>Salt</td>
<td>1200 lbs.</td>
<td>1800 lbs.</td>
<td>1200 lbs.</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>360 lbs.</td>
<td>360 lbs.</td>
<td>360 lbs.</td>
</tr>
<tr>
<td>Calcium formate</td>
<td>240 lbs.</td>
<td>240 lbs.</td>
<td>240 lbs.</td>
</tr>
<tr>
<td>Commercial chrome liquor</td>
<td>290 gal.</td>
<td>290 gal.</td>
<td>290 gal.</td>
</tr>
<tr>
<td>Bicarbonate</td>
<td>180 lbs.</td>
<td>180 lbs.</td>
<td>180 lbs.</td>
</tr>
</tbody>
</table>

ON 24,000 LBS. OF STOCK

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Saving 6.6% on Chromium Tanning Materials</td>
<td>19 gal. chrome liquor</td>
</tr>
<tr>
<td>Saving 33% on Salt</td>
<td>600 lbs. NaCl</td>
</tr>
</tbody>
</table>
THE RECYCLING OF CHROME TANNING LIQUORS

TABLE V
ANALYSIS OF SPENT SOLUTIONS

Sample: 4 Batches Chrome Composite

<table>
<thead>
<tr>
<th></th>
<th>Unfiltered</th>
<th>Filtered</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suspended Solids</td>
<td>6.194 mg./l. 0.348% 6.029 lbs./gal.</td>
<td>5.692 mg./l. 0.352% 0.030 lbs./gal.</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Salt</td>
<td>4.83 g./100 ml. 0.029 lbs./gal.</td>
<td>4.87 g./100 ml. 0.405 lbs./gal.</td>
</tr>
</tbody>
</table>

After working with the system for some time, it was decided that the quantity of chrome to be used in the tannage should not be decreased in accordance with the quantity used in the pickle. This resulted in an increase in the chrome fixed by the leather with no change in the quantity of the material used.

It was found that in discharging the chrome liquor from the processors it was best not to run the hide processors to extreme dryness. The chrome liquor should be pumped out well, with the leather lying in a static condition. This method avoided the mill grain effect. The system has worked very well, and this company has been producing leather on this basis for over eight months.

Stratigraphic analyses of the chrome leather produced shows good, even penetration in both tannages (Table VI). We are well satisfied with the quality of the leather.

TABLE VI
STRATIGRAPHIC ANALYSIS — % Cr₂O₃
(Hide Substance Basis)

<table>
<thead>
<tr>
<th>Layer (Number)</th>
<th>Recycle System</th>
<th>Regular System</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain</td>
<td>4.97</td>
<td>2.85</td>
</tr>
<tr>
<td>2</td>
<td>3.19</td>
<td>4.06</td>
</tr>
<tr>
<td>3</td>
<td>3.69</td>
<td>3.76</td>
</tr>
<tr>
<td>4</td>
<td>3.91</td>
<td>4.39</td>
</tr>
<tr>
<td>5</td>
<td>3.54</td>
<td>2.68</td>
</tr>
<tr>
<td>6</td>
<td>3.97</td>
<td>4.13</td>
</tr>
<tr>
<td>Flesh</td>
<td>4.27</td>
<td>4.40</td>
</tr>
</tbody>
</table>
Some additional savings could be obtained if sump pumps were arranged with the machine and the floor drains, but we have not gone into this additional complication since the quantity of chrome discharge is now within the acceptable limits.

ACKNOWLEDGMENTS

The authors would like to thank Fred Severance of Seal Tanning Company for his help and encouragement on this project, and also Julian Agoos of Seal Tanning for his permission to publish this work.

REFERENCES


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DISCUSSION

Mr. Raymond A. Hauck (Geo. Moser Leather Company; then at Tanners' Council Laboratory): Tom, I would like to thank you for bringing us a practical paper. The work presented today demonstrates again that recycling is practical as a means of reducing chrome in the prime tan effluent. Previously we have had reports on recycling chrome in the paddle and in the drum system. The current success in the hide processor certainly indicates that the recycle can be attained in normal tannery processes regardless of the equipment being used for chrome tannage.

In addition to reducing the chrome in the effluent, the results suggest that the step can save money on tanning material costs without adverse effect on leather quality. Tom, could you give us an overall estimate of the efficiency of this system?

Dr. Thomas C. Thorstensen: We are using approximately 1600 pounds of Cr2O3 per day. Without any recycling, we would be dumping about 320 lbs. Cr2O3 per day. With the present recycling we are dumping about 12 pounds of Cr2O3 per day.

Mr. Albert S. Jamison (Seton Leather Company): Tom, did you check your chrome in the total tannery effluent after this recycling?

Dr. Thomas C. Thorstensen: This is very difficult to do in this tannery due to the multiple sewer discharges in the old textile mill building which this tannery uses. There is no common discharge. However, we can estimate that figure based on the tannery use of 600,00 gallons of water per day. This means
that with a loss of 12 pounds of Cr₂O₃ per day or 8 pounds of chromium, we are down to 1.6 mg. chromium/liter.

Mr. Sigmund Panzer (Robson-Lang Leathers Ltd.): Did you secure any analytical data on formates in the recycled liquors?

Dr. Thomas C. Thorstensen: We did not analyze for formates. Similar principles of buildup to a stable level should result, and a saving in formate used could be possible.

Mr. Sigmund Panzer: Will the increase in formate level cause any difficulty?

Dr. Thomas C. Thorstensen: I do not expect any difficulty, and we have not seen any practical difficulties in the tannery operations or leather quality.

Mr. Panzer: Are many unfinished leathers marketed?

Mr. Thorstensen: Most of the leather is made from heavy steerhides and marketed as finished side leather.

Mr. Panzer: Have you observed any darkening of the blue stock as you continue recycling?

Mr. Thorstensen: No, we did not see any change as we entered the recycling process. All tanning is now run on recycled liquors without any periodic dumping of liquors. Even so, the blue color still seems entirely normal.

Mr. Panzer: What about the chrome you precipitate?

Dr. Thorstensen: This precipitated chrome is not reused.

Mr. Panzer: We have been experimenting with a similar recycle system. We make a wide variety of unfinished leathers. We have observed a darkening of the color, which plays havoc with our colors.

Dr. Thorstensen: This has not been our experience. The chrome tanned stock in this tannery is not significantly darker than the chrome tanned stock you see in other tanneries, in my opinion.

Mr. Satyendra M. De (Chestnut Operating Company): We have been working on chrome recycling. In suede leather we found color darkening after tannage. Have you tried suede leathers?

Dr. Thorstensen: We have not seen this color darkening. The tannery does not make suede leather.

One possible cause of color darkening could be fat buildup in the chrome tanning liquors. This would be accentuated in suede leather. Since we do draw off the accumulated grease, we may be avoiding this problem.

Mr. De: We thought of that also.

Mr. Raymond A. Hauck: Thank you, Tom, for a very interesting practical paper.