# RECYCLING OF LIME UNHAIRING AND CHROMIUM SOLUTION

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**Abstract**
Over the years calcium hydroxide and Sodium Sulphide have been used in or unhairing processes. From The three pits system through the short float hair destruction, yet The spent solution has caused a significant, pollution problem. Sharphouse and other workers have shown that the old used lime liquor becomes stronger unhairing agent due to the breakdown of the disulpide link in the hair and The hair roots. This fact leads to the reuse of spent lime solution and recycling after topping the same solution with sulphide and calcium hydroxide. Using and recycling of spent lime solution with the required topping, the pelts were processed from liming through dried crust. The crusts were subjected to physical analysis of tensile strength of 265kg/cm2 and average elongation of 65%and thickness of 1mm. These properties are proved to be satisfactory and well compared with SSMO NO (2016:579) The recycling has been carried out to, ten runs, in each run the hair is satisfactory removed.it is concluded that the recycling can be run indefinitely with subsequent cleaning of filtered cake. The quality of The leather processed is normal with an advantage of environmental protection and saving in chemicals and water. The same procedure was used for chrome recycling for ten times and the leather processed through recycling is proved to be well within SSMO standard.

**Keywords:** spent lime, old lime liquor, chemicals saving, environmental protection

## Introduction

Tannery waste water effluent has high BOD, COD .and high TSS. Tannery waste water is treated biologically, in aerobically, anaerobically or chemically. The process of treatment in this manner is expensive and difficult to reach The SSMO standard, on the other hand it is reported that lime liquors strengthen with time and that limes solution were reused 20 times in succession without any treatment to remove soluble proteins or solids. It is also reported that lime-sulphide unhairing liquors can be recycled more than 20 times, perhaps indefinitely. The only treatments necessary before re-use are temperature adjustment and replenishment with lime, sulphide and water. Recycling of lime liquors has no apparent effect on leather quality or yield. This method could be developed as no-float system of unhairing. Even if the liquors are discharged after 20-fold use, there can be overall, 20- fold reduction in water consumption, lime and sulphide.

Fine screening of the residual float removes from the re-circulated liquor a substantial amount of organic matter. On the whole, 30 to 40% of the COD and 35% of the nitrogen may be eliminated from the mixed effluents.

## Methodology:

In this research all the work was carried out experimentally. The experiments were designed to recycle the spent solution from the process of lime-unhairing and chrome tonnage. The tanning processes were applied using standard recipe.

**Lime-unhairing process**

After soaking, the process of lime-unhairing was applied. Based on soaked weight 300%water (tap water) and 4% sodium sulphide ( ) were added, then soaked skins were added to the solution, they were run for 1 h and then 4% calcium hydroxide ( ) was added, paddle was run for 1 h, it was run 10 min per h for 4 h, they were left O/N, and pH =12 was obtained and. complete hair removal was confirmed.

Remaining unhairing liquor was filtered by screen and saved for next trial.

The volume of remaining unhairing liquors was measured and the water volume was completed to 300% based on soaked skin weight. The real volume of water was calculated using the following equations:

Total weight of fresh water to be added (VT):

$$W_T \ (kg) = \frac{300}{100} * \ soaked \ skin \ weight (kg)$$

$$V_T \ (L) = \frac{W_T \ (kg)}{\rho \ (\frac{kg}{L})}$$

* $\rho$ is density of water, assumed to be $1 \ \frac{kg}{L}$

Volume of water that is added to adjust the amount required (V):

$$V(L) = V_T \ (L) - V^* \ (L)$$

The remaining amount of $Na_2S$ and $Ca(OH)_2$ in filtered remaining unhairing liquors was assumed to be 30% based on soaked skin weight in previous trail. Thus the amount of $Na_2S$ and $Ca(OH)_2$ was calculated by following equations:

Saved amount of $Na_2S$ and $Ca(OH)_2$:

$$X^* = \frac{30}{100} * Na_2S \ weight \ ^*$$

$Na_2S \ weight \ ^*$: This is the weight of $Na_2S \ or \ Ca(OH)_2$ in previous trial.

The total amount of $Na_2S$ and $Ca(OH)_2$ that are added:

$$X_T = Soaked\ skins\ weight$$

Amount of $Na_2S$ and $Ca(OH)_2$ that to be added:

$$X = X_T - X^*$$

The volume of water and amount of that are added to adjust the amount required were added to the remaining unhairing liquors from previous trail, then soaked skins were added to the solution, paddle was run for 1 h. Then real amount was added, it was run for 1 h, run for 10 min per h for 4 h, skins were left in unhairing liquors O/N, and pH =12 was confirmed. Complete hair removal process was confirmed. Remaining unhairing liquor was filtered by screen and saved for next trial. This process of recycling was repeated 10 times.

Tanning and basification processes

After re-liming, fleshing, de-liming, bating, and pickling processes were done, tanning process was applied. Based on fleshed weight and in same pickling solution 8% basic chromium sulphate was added in two portions, drum was run for 4 h each portion was run for 2 h, pelts were left in tanning solution O/N, and in same tanning solution 1% sodium bicarbonate was added in three portions after dilution with water ( ), each portion was run for 15 mints, pH between ( ) and boiling test were confirmed.

The volume of remaining tanning solution was measured and the water volume was completed to 100% based on fleshed skin weight. The real volume of water was calculated the using following equations:

$$Saved\ water\ volume = measuring\ volume = V'(L)$$

Total volume of water to be added (V ):

$$W°(kg) = \frac{100}{100} * soaked\ skin\ weight\ (kg)$$
$$= soaked\ skin\ weight\ (kg)$$

$$V°\ (L) = V° \frac{(kg)}{\rho\ (\frac{kg}{L})}$$

\* $\rho$ is density of water, assumed to be $1\ \frac{kg}{L}$

Volume of water to be added (V):

$$V\ (L) = V°\ (L) - V'\ (L)$$

The pH of remaining tanning solution is between ($4.0 - 4.5$), therefore formic acid is to adjust the pH between ($2.8 - 3.0$).

Based on fleshed weight 0.5% Formic acid was added to tanning solution (after water volume was completed) in three portions after dilution with water (1:10), each batch may run for 10 mint, pH between $2.8 - 3.0$ was maintained.

The remaining amount of $Cr(OH)So_4$ in the remaining tanning solution was assumed to be 30% based on fleshed skin weight in previous trail. Thus the required amount of $Cr(OH)So_4$ was calculated by following equations:

$$X' = \frac{30}{100} * Cr(OH)So_4 \ weight$$

The total amount of $Cr(OH)So_4$ that to be added:

$$X° = fleshed \ skins \ weight \ * \frac{8}{100}$$

Amount of $Cr(OH)So_4$ that is added:

$$X = X° - X'$$

After pH was adjusted been between ($2.8 - 3.0$), fleshed skins were added to the solution, and real amount of $Cr(OH)So_4$ was added in two portions, each portion was run for 2 h, pelts were left in tanning solution O/N. basification process was done and pH between ($4.0 - 4.5$) and boiling test were confirmed. Shaving and re-tanning processes were done to produce crusts. Physical and chemical tests were done on crusts.

**Chrome recovery**

Basic chromium sulphate in remaining tanning solution was specified using calibration chart, this chart was drawn by taking pickle solution (pH = 2.8) and various weight of basic chromium sulphate were dissolved in above solution, and at each weight of basic chromium sulphate Baume reading was taken.
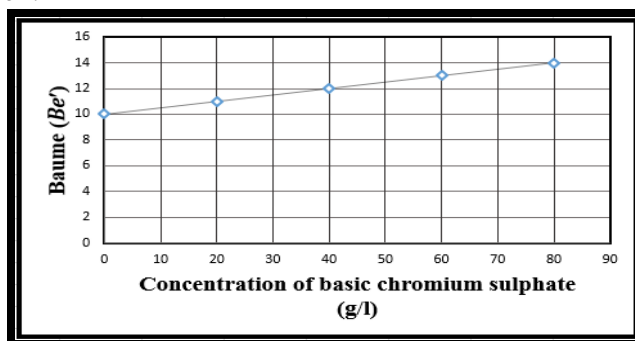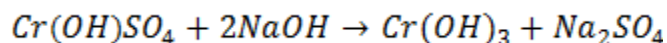
Figure 1: Calibration chart for basic chromium sulphate

After that sodium hydroxide was added to the remaining tanning solution. Sodium hydroxide that must be added was specified according to following chemical reaction:

$$Cr(OH)SO_4 + 2NaOH \rightarrow Cr(OH)_3 + Na_2SO_4$$

Sodium hydroxide was added and thoroughly mixed, after 24h chromium hydroxide was precipitated and the dyer Baume read was taken.

Distilled water was added to sample of chromium hydroxide cake, concentrated sulphuric acid was added to this solution until (pH  ), the volume of concentrated sulphuric was taken.

**Results and Discussions**

Experimental trials were run for recycling of lime-unhairing solutions and spent chromium sulphate solution for 10 times, in each case the residuals (water, lime, sodium sulphide and basic chromium sulphate) were calculated and each run was topped with the required make-up.

From table (1) the percentage of water saved was in the range (60% - 80%), the percentages of sodium sulphide and calcium hydroxide saved were assumed to be 30% (Mohammed, 2003). The amount of sodium sulphide found in the used liquor is due to the amount that was not reacted, in addition to the fact that pulping reaction induced by sodium sulphide had produced sludge containing keratin sulphide reaction products. As calcium hydroxide has a limited solubility of 0.125 %, undissolved lime remains in solution.

The percentage of hair removal is 100% for both control and recycled pelts. From table (2) the percentage of water saved was in range (85% - 70%), the percentage of basic chromium sulphate saved was assumed to be 30%. The amount of basic chromium sulphate found in the used liquor is due to the amount unreacted. The percentage of shrinkage in boiling test is 0% for both control and recycled W/B. Therefore, the recycling method minimizes the amount of water, sodium sulphide and calcium hydroxide used, thus minimize the environmental effect of tannery waste water and minimize operation cost of unhairing-lime process.

From tables (3) and (4) the physical and chemical properties for both controlled and recycled crusts were in conformity with standards of SSMO and there were no significant differences between controlled and recycled crusts.

Basic chromium sulphate recovery process was done in efficiency of 99% (BAT, 2013) reported values, measured as total chromium in a daily composite sample, after sedimentation or flotation of the separate chromium-containing effluent before mixing, are 1 – 2 mg Cr/l.

Direct recycling of basic chromium sulphate is better than precipitation and separation method for the following reasons:

1.    There was little amount of chrome in filtrate produced by indirect recycle.

2.    Direct recycling did not produce any waste-water, filtered water produced by indirect recycle must be treated before it is discharged.

3.    Direct recycling minimizes the amount of water used.

4.    Precipitation method has high production cost compared with direct recycling method.

Table (1): Results of lime- unhairing process

| Trial No. | Soaked skins weight (kg) | Water 300% | | Sodium sulphide (4)% | | Calcium hydroxide (4%) | | pH | Unhairing efficiency |
|---|---|---|---|---|---|---|---|---|---|
| | | Saved * (L) | Added (L) | Saved* (g) | added( g) | Saved*( g) | Added (g) | | |
| 1 | 11 | - | 33 | - | 440 | - | 440 | 12.0 | Satisfactory |
| 2 | 10 | 22 | 8 | 132 | 268 | 132 | 268 | 12.0 | Satisfactory |
| 3 | 10 | 16 | 14 | 120 | 280 | 120 | 280 | 12.0 | Satisfactory |
| 4 | 12 | 20 | 16 | 120 | 360 | 120 | 360 | 12.5 | Satisfactory |
| 5 | 10 | 28 | 2 | 144 | 256 | 144 | 256 | 12.3 | Satisfactory |
| 6 | 11 | 20 | 13 | 120 | 320 | 120 | 320 | 12.0 | Satisfactory |
| 7 | 11 | 25 | 8 | 132 | 308 | 132 | 308 | 12.5 | Satisfactory |
| 8 | 10 | 23 | 7 | 132 | 268 | 132 | 268 | 12 | Satisfactory |
| 9 | 12 | 18 | 18 | 120 | 360 | 120 | 360 | 12.3 | Satisfactory |
| 10 | 10 | 28 | 2 | 144 | 256 | 144 | 256 | 12.5 | Satisfactory |

Saved* is the amount of component was saved from previous trails

Table (2): Results of tanning process

| Trial No. | Fleshed skins weight (kg) | pH* | Water 100% | | Basic chromium sulphate 8% | | pH** | Boiling test |
|---|---|---|---|---|---|---|---|---|
| | | | Saved * (L) | Added (L) | Saved* ($g$) | Added ($g$) | | |
| 1 | 6 | 2.8 | - | 6 | - | 480 | 4.5 | Pass |
| 2 | 5 | 2.8 | 5 | - | 144 | 256 | 4.5 | Pass |
| 3 | 5 | 2.8 | 4 | 1 | 120 | 280 | 4.5 | Pass |
| 4 | 7 | 2.8 | 4 | 3 | 120 | 440 | 4.3 | Pass |
| 5 | 5 | 2.8 | 5 | - | 168 | 232 | 4.5 | Pass |
| 6 | 6 | 2.8 | 4 | 2 | 120 | 360 | 4.0 | Pass |
| 7 | 6 | 2.8 | 5 | 1 | 144 | 336 | 4.5 | Pass |
| 8 | 5 | 2.8 | 5 | - | 144 | 256 | 4.5 | Pass |
| 9 | 7 | 2.8 | 4 | 3 | 120 | 440 | 4.5 | pass |
| 10 | 5 | 2.8 | 3 | 2 | 168 | 232 | 4.5 | pass |

Saved* is the amount of component was saved from previous trails.

Table (3): Results of physical tests

| Trial No. | Thickness mm | Tensile strength Kg/cm$^2$ | Elongation % |
|---|---|---|---|
| 1 | 1 | 265.0 | 70 |
| 2 | 1 | 261.0 | 67 |
| 3 | 1 | 263.5 | 69 |
| 4 | 1 | 255.0 | 65 |

| 5  | 1 | 258.0 | 62 |
|----|---|-------|----|
| 6  | 1 | 261.5 | 66 |
| 7  | 1 | 257.5 | 61 |
| 8  | 1 | 254.0 | 63 |
| 9  | 1 | 255.0 | 60 |
| 10 | 1 | 251.0 | 61 |

Table (4): Results of chemical analysis

| Trial No. | Moisture % | Ash % |
|-----------|------------|-------|
| 1  | 6.0 | 1.50 |
| 2  | 5.5 | 1.54 |
| 3  | 6.0 | 1.57 |
| 4  | 5.0 | 1.52 |
| 5  | 4.5 | 1.50 |
| 6  | 4.5 | 1.53 |
| 7  | 5.0 | 1.58 |
| 8  | 4.5 | 1.54 |
| 9  | 5.0 | 1.55 |
| 10 | 5.0 | 1.60 |

**Result of chrome recovery:**

From the calibration cure the composition of spent basic chromium sulphate = 20g/l
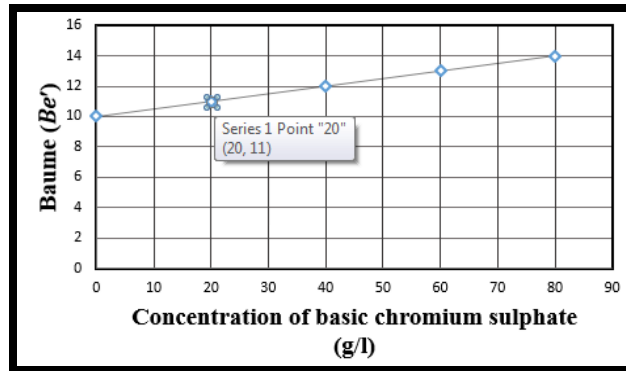
Figure 2: Calibration of chrome composition vs reading

$$y(g) = \frac{x(g) * 80}{152}$$

$$y = \frac{20(g) * 80}{152} = 10.53 \ g$$

y (g) is the theoretical amount of   that must be added,   was added according to following equation:

$$y'(g) = y(g) + \ 0.1 * y(g)$$

$$y'(g) = 10.53 \ g + \ 0.1 * 10.53 \ g = 11.583 \ g$$

15 ml of distilled water was added to 85 g of chromium hydroxide cake, after adding 1.9 ml of concentrated sulphuric acid pH =1.5 and basic chromium sulphate was precipitated.

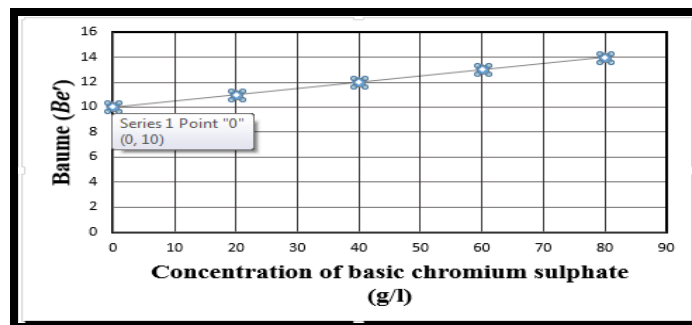From the calibration cure the composition of spent basic chromium sulphate  g/l



Figure 3: Chrome composition vs reading after filtration

**Recommendations:**

Based on results obtained from recycling of lime-unhairing and spent solution of basic chromium sulphate which showed good physical and chemical properties of crusts, minimized pollution and production cost, the following are recommended:

1. Recycling in other processes including soaking, liming, de-liming and re-tanning.

2. Cost analysis of recycling processes.

3. Hair-saving method application to save the hair and to reduce the cost of processing.

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