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Recycling of Pickling Solution

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Abstract

The aim of this research is to recycle the spent pickling solution to reduce the effect of pollution to the environment and to minimize the cost of pickling operations by saving water and chemicals compared to the conventional method without any influence of the quality of the produced leather. It has been found on the basis of this work, that average savings were 42% water, 42% salt, 19.9% H_2SO_4 and 20.9% formic acid in addition to the protection of the environment. Raw sheep and goat skins in the stage of liming were processed with the normal pickling recipe and the once-used pickling solution was analyzed for salt and acid contents. To make-up the same concentration of the fresh liquor acids and sodium chloride were added to prepare new liquor for recycling. This process was repeated three times. After the end of each operation the pelts were assessed, analyzed, the pH of the cuts were taken and the results were found to be satisfactory. Then the pelts were turn her processed to the crust and analyzed for physical tests, the results were reasonable. The leather produced is normal, soft and full with good break and good tensile strength. The resultant leather has similar properties as the one produced with the conventional method. The physical tests include the tensile strength, Flexometer, Lastometer, Water Penetration, as shown in tables, (5) to (16). This process of recycling is recommended to be applied gradually in the tanneries. Extensive researches are ongoing in Italy, Australia and other countries on recycling of tannery effluents. This is because there is a save in chemicals and reduction in pollution hazards. Its application is simple and requires a collection pit, a filter, a pump and a pipeline to and from the drum.

Keywords: *Pickling, Recycling, Tanners, Leather.*

I. Introduction

Tanners employ a variety of raw materials to produce the leather required for the use of modern society. Hides and skins of the principle species of domestic animals such as Cattle, Buffalo, Goat and Sheep are converted into various types of leathers.

Hides and skins were obtained regularly in commercial quantities, as meat is a daily food requirement in the entire world, hides and skins become available as by-products of the meat industry and it has become a necessity to preserve and utilize them properly for social and economic benefits and pollution control.

Sudan has very large resources of hides and skins. This is due to the huge livestock population. This is estimated to be 124.7 million, hides and skins in the year 2000. (3)

Approximately 4.68 million cattle hides, 10.979 million sheep skins, 10.421 goat skins and 100 thousand camels, is remarkable for possessing a combination of properties to be found in no other natural or man – made material. When properly processed will resist decay, became flexible and strong it with a unique porous structure which enable it to "breath", that is, to permit the passage of air through it as well as water vapor, it can be easily worked, cut, joined, and stretched, embossed, dyed and glazed a characteristic which for some purpose make it superior to woven materials.

Pickling process is rather important for preservation and preparation of hides and skins for the following process such as chrome tannage and retannage. In this process expensive and polluted chemicals such as sulphuric, formic acids, salt and water were used in considerable quantities.

The aim of this work is to recycle the pickling solution in order to save these polluted chemicals and in order to protect the environment. To realize the application, the solution needs to be filtered, analyze for acid, salt and water content. A make-up to these chemicals is required to give the same level of the conventional method in use, it is

hoped that the required level would give an acceptable quality.

To make this true the pelts are proposed to be processed through pickling up-to the crust. The crusts produced have to be physically and visually assessed.

Pickling

The treatment of delimed or bated pelts with a solution of acid and salt is known as pickling. This is the most important and essential operation prior to mineral tannage, but stock selected for vegetable tannage generally does not require such acid-salt pretreatment. Now-a-days it is strongly supported that by proper adjustment of acid and salt in this pickling operation a large amount of hydrolysable tannin can be easily reduced in the product. In short, the main objectives of this pickling operation are to bring the delimed or bated pelt to a required degree of acidity so that the subsequent tannery operations can be smoothly and scientifically controlled. If delimed or bated pelts, as for example, are directly put into chrome liquor without going through the pickling operation the pelts will first of all absorb the free acid of the liquor till the protein becomes acid-saturated. When the acid binding capacity of the protein at that pH value of the chrome liquor is satisfied, it is the chrome compound which will penetrate and tan the collagen fibers. The binding capacity of the bated or delimed collagen is therefore fully satisfied, according to the free acid content of the chrome liquor, in this pickling operation before the stock is taken for mineral tannage. It is really painful to mention that no fruitful and scientific research has yet been carried out to determine the effect of pickling variables on leather quality. A large number of practical tanners of America were asked to provide answers to some of these questions based on their experience, but sorry to say that their answers were so much contradictory and diverging in nature that no final conclusion could be drawn. Though this pickling operation is very simple and in most cases sulphuric acid and common salt are used but the proportions of acid, salt and water in pickle bath and the method of pickling vary considerably. Some tanners, as for example, prefer short pickling; some again pickle their pelt up to the state of equilibrium. Similarly somewhere salt is added first and then the acid, somewhere both acid and salt are added together. One tanner may prefer higher percentage of acid in chrome liquor whereas his fellow tanner may prefer the opposite. A brief and scientific investigation should therefore be made in this chapter from the experimental results obtained by Theis, McLaughlin and others. (5)

Objectives

*To recover and save the water, salts and acids for the pickling process.
*To protect the environment from these polluted chemicals.

II. Materials and Methods

Process of Pickling Recycling

4 pieces of skins, 1 of sheep and 3 of goats were weighed and based on this weight200% of water was added, 8% salt were added, run for 30 minutes, 1.2% H_2SO_4 (diluted 1:10) and 0.5% formic acids were added, run for 2 hours after checking the pH to be in the range of 1.5 – 2.5, this was the once-used solution. This spent solution was analyzed for salt and acid contents by refractometer and adjusted to the required level, and the skins were pickled by the same procedure. Then the spent solution was analyzed for salt and acid content and adjusted up to the required level of 8% salts, 1.2% H_2SO_4 and 0.5% formic acids. The same was repeated three times.

pH

The pH was measured by pH meter and pH paper for the pickling solution before recycling and after each treatment for all the four experiments and chrome solution.

Methods

Experimental Procedures

Experiments have been carried out in the incubator at Sudan University.

The aim of the Study is to investigate the process of recycling of the pickling solution the spent solutions from the process were treated by the following

manner; recycling experiments the fresh solution of the normal recipe were carried out . The spent solution was re-used, and repeated for three times, and the results were shown in tables (2, 3).

Physical Analysis

Preparation of Sample

The pieces for physical tests were cut from the official sampling position (HGJK) and from shoulder (1)

Condition:

The specimens for physical testing were kept in standard atmosphere at temperature 20±2c relative humidity 65%±2% during 48 hours immediately preceding its use in test.

Measurement of Thickness

The specimens were placed in the standard dial micrometer gauge with grain side up with applied loading 500g/cm2 at the presser foot .The thickness of the leather was measured in four positions at least 1cm from the edge, and the time of dwell was 5 seconds before taking reading , The mean value of thickness was calculated. The diameter was measured in two positions at right angles using veneer calipers on the flesh and grain sides'. The mean diameter (cm) was calculated.

1. Measurement of Tensile and Percentage Elongation

i) Tensile Strength

The tests are indented to be used with all kinds of leather. The same specimen may be used to carry out any or all of the tests. The samples were cut parallel and perpendicular to the backbone using a dumbbell shape.

Calculation:

$$\text{Tensile strength} = \frac{\text{Maximum Breaking Load}}{\text{Cross-sectioned area}}$$

Unit's N/mm^2

ii) Percentage Elongation at Break:

The initial free length between the clamps before and after final free length was set at 5cm and the elongation calculated.

Calculation:

$$\text{Elongation, \%} = \frac{\text{Final Free Length} - \text{Initial free length}}{\text{Initial free length}} \times 100$$

2. Flexometer

Condition rectangular test specimens of size 70 × 45 from sampling location and clamp test piece in the Bally Flexometer or its equivalent and switch on. Assess the damage of the finish grain using a magnifying glass at every 10,000. Terminate the experiment after 100.000 flexes.

3. Grain crack load and distention (Lastometer Test)

Cut three specimens of 44.5 mm .diameter from the sampling location of shoe upper leather. Condition them for 48 hours at 20oc and 65%R.H. Clamp to test specimen tightly in the lastometer and force the plunger at the rate of 0.20±0.05 mm /second. This is done by turning the hand wheel clockwise at one revolution per second. When the crack appears note down the force and distention.

Calculation:

$$Penetrating\ Strengrh = \frac{Load}{Thickness}\ (kg/cm)$$

4. Resistance to Water Absorption (Bally)-Dynamic Method

Take four rectangular pieces of leather 75× 60mm, (two from each direction) from the sampling location and condition the test pieces. Buff the grain surface on a piece of grade 180 emery paper. Press the test piece against emery with a load of 1 kg uniformly distributed over the surface of leather and moves the test piece 10 times backward over the emery paper.(1)

To determine the amplitude of crack motion to be used, clamp the test piece in the auxiliary apparatus

with cylinders 40mm. apart .Condition the test piece mechanically by moving one cylinder 2mm. closer to the other (equivalent to5% reduction in length) at a speed of approx 2mm. in five seconds. Withdraw the cylinder at the same speed to the original position and again advance it to give 5% reduction in length is 10% (4mm) instead of 5% (2mm) .If the mean value of the two loads at 5% and 10% reduction exceeds 10 kg then use5% amplitude for water penetration test. If mean value lies between 5kg and 10kg then use 7.5% amplitude for the test .If the mean value is less than 5kg make further measurement with reduction of length 15% (6mm) instead of 5% or 10 % . If the mean value of 5%, 10% and 15% reduction of length exceeds 2 kg use 10% amplitude crank for penetration test and if below 2 kg the use 15% amplitude crank for penetration test.

Set the water resistance testing machine (Penetrometer) to give required amplitude. Weight the sample of leather (w1) .With two cylinder maximum apart, fix the test piece to the cylinder with ring clamps t, from the trough. The outer surface of the trough should be grain layer or the layer that forms the outer surface of the shoe. Insert the brass or copper turnings inside the trough and lower the electrode plate to make contact. With the turning raise the water tank and make sure that the level lies 1cm below the top of the cylinders.

Start the motor and measure the time required for first sign of penetration of water trough leather specimen so indicated by appearance of light on indicator lamp. At the end of the interval during which water absorption is to be measured , stop the motor remove the test piece , lightly to remove adhering water and weight (w2). If quantity of water penetrated is measured replace the test piece as quickly as possible from the trough without brass tunings. Weight an absorbent cloth (w3) and place it in the trough formed by the sample. Replace the electrode to rest on the cloth and run the machine. At the end of 30 min interval remove the cloth and reweigh (w4).

Calculation:

$$\text{Water absorbed} = \frac{W2 - W1}{W1} \times 100$$

Amount of water penetration at given time = W4 – W3

III. Results and Discussions

Results-Experiments were carried out to determine the effect of recycling on leather quality. The experimental work was commenced with a calibration carve shown in table and figure (1). Other experiments covered the recycling and physical testing as shown in tables (2) to (16).

Table 1: Calibration of Salt Content

Concentration of salt (mg/ml)	R.I
0.0	0.0
0.01	17
0.02	35
0.03	43
0.04	68
0.05	84
0.06	100

0.07	119
0.08	133
0.09	148
0.1	165

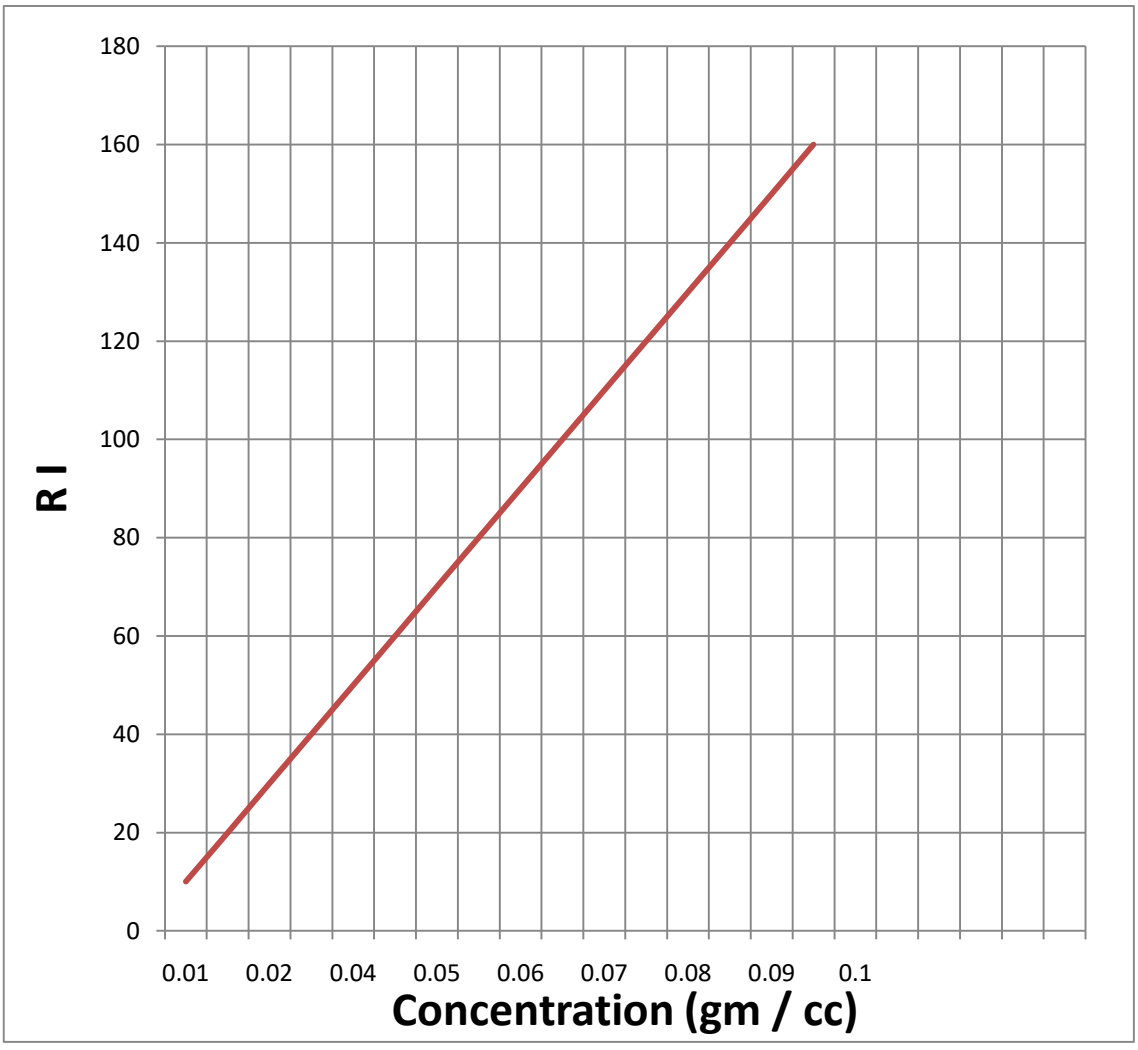

Figure 1: Calibration of Salt Content vs. Refractometer Index (RI)

Table 2: Chemical Analysis of Fresh Liquors

	Weight (g)	Salt	H_2SO_4 Acids	Formic
Fresh	600	8%	1.2%	0.5%

Table 3: Total Percentage of Salt, H_2SO_4 and Formic Acids of Recycled Liquors before make up

	Weight skin(g)	Salt %	H_2SO_4 Acids %	Formic %
Cycle 1	900	5.13	0.78	0.41
Cycle 2	400	3.6	0.64	0.33
Cycle3	600	3.9	0.64	0.33

Table 4: Conventional Pickling Method versus Recycling Method

	Consumption without recycling (gm)	Net consumption with recycling (gm)	Saving %
Water	**5000**	**2900**	**42**
Salt	**200**	**116**	**42**
H_2SO_4 Acids	**30.3**	**24.26**	**19.9**
Formic	**12.5**	**9.883**	**20.9**

Tensile Strength=Load/Area (N/mm^2)

Sample (1):

Area of Section Sample = Width $\times$ Thickness

Thickness = 1.083
Width = 10mm

Area = 1.083mm $\times$ 10mm = 10.83 mm^2, the Length of Sample = 50mm

Table 5: Tensile Strength for Sample $(\|, 1)$

Length (mm)	Increase of Lengths (%)	Load (kg)	Load (N)
0	16.9	0	0
2	17.1	4.6	45.13
4	17.3	6.8	66.71
6	17.5	10.3	107.04
8	17.7	12	117.72
10.5	17.95	12	117.72

Elongation Percentage:

$$\% \Delta L = \frac{(17.95-16.9) \times 10\ mm}{50\ mm} \times 100$$

Table 6: Tensile Strength for Sample $(\perp, 1)$

Length (mm)	Increase of Length (%)	Load (kg)	Load (N)
0	16.8	0	0
2	17.0	.8	7.85
4	17.2	1.5	14.72
6	17.4	2	19.62
8	17.6	2.4	23.54
10	17.8	2.5	24.53
12	18.0	2.8	27.67
14	18.2	3.2	31.39
16	18.4	3.6	35.32
18	18.6	4.1	40.221
20	18.8	4.7	46.107

22	19.0	5.2	51.012
24	19.2	5.9	57.88
26	19.4	6.5	63.77
28	19.6	7.2	70.632
30	19.8	7.2	70.632

Tensile Strength (N/mm^2) = $\frac{70.632\ N}{8.83\ mm^2} \cong$ **8 N/mm^2**

Area = 10 mm $\times$ **0.88 mm = 8.88 mm^2**

Table 7: Tensile Strength for Sample $(\|, 2)$

Length (mm)	Increase of Length (%)	Load (kg)	Load (N)
0	16.9	0	0
2	17.1	1.3	12.75
4	17.3	1.3	12.75
6	17.5	1.3	12.75
8	17.7	1.3	12.75
10	17.9	1.3	12.75
10.2	18.1	1.6	15.7
10.4	18.3	2.2	21.58
10.6	18.5	2.8	27.47
10.8	18.7	3.5	34.34
11	18.9	4.4	43.16
11.2	19.1	4.7	46.11
11.4	19.3	5.5	53.96
11.6	19.5	5.5	53.96
11.8	19.7	5.5	53.96

12	19.9	6.5	63.77
12.2	20.1	6.5	63.77
12.4	20.3	7.3	71.61
12.6	20.5	7.8	76.52
12.8	20.7	8.2	80.44
13	20.9	9	88.29
13.2	21.1	9.8	96.14

Table 8: Tensile Strength for Sample $(\perp, 2)$

Length (mm)	**Increase of Length (%)**	**Load (kg)**	**Load (N)**
0	16.9	0	0
2	17.1	1.5	14.72
5	17.4	7.6	74.56
6.5	17.55	9	88.29
8	17.7	10.8	105.95
10	17.9	12.4	121.64
10.2	18.1	14.7	144.21
10.4	18.3	16.8	164.81
10.6	18.5	18.2	178.54
10.7	18.6	18.5	181.49

Table 9: Tensile Strength for Sample $(\parallel, 3)$

Length (mm)	Increase of Length (%)	Load (kg)	Load (N)
0	17.1	0	0

1	17.2	0.9	88.3
3	17.4	2.6	25.51
5	17.6	4.4	43.16
7	17.8	6.6	64.75
9	18	9	88.29
10.1	18.2	11	107.91
10.3	18.4	12.7	124.59
10.5	18.6	14.7	144.21
10.7	18.8	16.5	161.87
10.9	19	19.8	194.24
11.1	19.2	22	215.82
11.4	19.5	24.4	239.36

Table 10: Tensile Strength for Sample $(\perp, 3)$

Length (mm)	**Increase of Length (%)**	**Load (kg)**	**Load (N)**
0	16.9	0	0
2	17.1	1.9	18.64
4	17.3	3.6	35.32
6	17.5	5.5	53.96
8	17.7	6.7	65.73
10	17.9	8	78.48
12	18.1	9	88.29
14	18.3	9.2	90.25
16	18.5	10.4	102.02

18	18.7	10.5	103.01
20	18.9	11.5	108.89
22	19.1	12.5	122.63
24	19.3	13.7	134.4
26	19.5	15	147.15
28	19.7	15	147.15

Table 11: Tensile Strength for Sample $(\|, 4)$

Length (mm)	Increase of Length (%)	Load (kg)	Load (N)
0	16.9	0	0
2	17.1	5.5	53.96
4	17.3	12.3	120.66
6	17.5	15.5	152.06
8	17.7	19.1	187.37
10	17.9	20.1	205.03
12	18.1	21.5	210.92
14	18.3	25	245.25
16	18.4	25	245.25

Table (12): Tensile Strength for Sample $(\perp, 4)$

Length (mm)	Increase of Length (%)	Load (kg)	Load (N)
0	16.9	0	0
2	17.1	1	9.81
4	17.3	2.3	22.56

6	17.5	4.7	64.11
8	17.7	6.9	67.69
10	17.9	9.3	91.23
12	18.1	9.8	96.14
14	18.3	10.5	103.01
16	18.5	11.9	116.74
18	18.7	12	117.72
20	18.9	13.1	128.51
22	19.1	14.8	145.19
24	19.3	16.4	160.88
26	19.5	18	176.58
28	19.7	18.5	181.49
30	19.9	19	188.35

Lastometer

Table 13: Thickness for Different Samples

Sample	Thickness (mm)	Sample	Thickness (mm)
1	0.9	**1`**	0.9
2	1.3	**2`**	1.3
3	1.2	**3`**	1.5
4	1	**4`**	1.1

$$\textit{Penetrating Strength} = \frac{Load}{Thickness}\ Kg/cm$$

Table 14: Lastometer Tester

Exp. No	Length (mm)	Load (kg)
1	8	8
1`	8	6
2	11	14
2`	8	11
3	9	13
3`	11	14
4	8	11
4`	9	13

Flexometer Tester

Table 15: Flexometer Test at 23000 feet

Sample No.	Result
Sample 1	Loss in grain Side
Sample 2	No defect
Sample 3	No defect
Sample 4	No defect

Penetrometer Tester

Table 16: Penetrometer Test for Different Samples

Sample	Absorption Time (s)	Water Absorption %
1	100	62
2	120	220
3	120	80
4	200	247

Discussions

The limed sheep and goat skins were processed and until pickling. The container was unloaded and the once-used pickling solution was filtrated and analyzed for acids and salt content. The amount of float was also measured.

Based on the weight of skins to the processed in the second experimental using the once-used pickling solution and based on the recipes of fresh batch, the amount of a make-up-salt acid and water were calculated and added loaded together. The delimed pieces were put in to the prepared solutions until the conditions of PH were realized the same was repeated for the third and four cycles.

- The Leather produced was processed through chrome until the crust. The physical test such as tensile strength, Flexometer, Lastometer and Water Penetrations, were carried out. The results of the Physical test were compared with standard of these tests and found to be satisfied **,** as shown in table(5) through (16)**.**
- From the proceeding results of the physical tests, it is clear that the recycling of pickling process can be used without affecting the quality of the leather produced. Although the recycling was carried out for three recycles, it obvious that it can be used for more cycles and perhaps indefinitely. The application is simple and needs only a tight control on the amount of acid and salt. The environmental will also be protected and clean production will be realized.

IV. Conclusion

Recycling of pickling solution can solve some of environmental problems. Firstly, the process leads to creation of clean technology and healthy environment. Secondly, reduction of the total cost of the pickling operation by saving in chemicals and water used.

Leather processed through recycling gave very acceptable quality, these were shown by physical, and visual assessment.

Before starting each recycling process, solid must be removed and the solution was to be topped with a make-up to level 8% of salt, 1.2 % of sulphuric acid, 0.5% formic acid and 200 % water.

V. Recommendations

The process of recycling of pickling solution is recommended to be adopted and applied in all Sudanese tanneries. The study that leather produced from the recycled pickling solution falls within the standard specifications. Its recommended that the recycling system applied in this work to be generalized and adopted in Sudanese tanneries.

VI. Acknowledgement

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