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Utilization of Improved Indigenous Tannins of Grain Powder (*Acacia Nilotica*) in Eco Friendly Tannage

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Abstract

New tanning mixture was investigated to improve the performance of indigenous tanning materials. Many experiments were conducted in National Leather Technology Centre, Sudan using a blend of 80% Acacia nilotica pods 'Garad' and 20% azadirachta indica 'Neem' barks. The spray-dried powder from a mixture of Acacia nilotica pods and azadirachta indica 'Neem' was applied for full vegetable tanning to produce shoe upper leathers. The physico-mechanical properties of the improved tanned leather were compared with conventionally tanned leather. The pretannage and full vegetable tannage were preceded using accustomed method in NLTC, Sudan while physio-mechanical analyses of the leather were performed using AOAC (1996). Parameters of the tanned leather were tensile strength (20.0 N/Cm^2), tear strength (4.4 N/cm), stitch tear strength (11.8 N/cm), elongation (40.5%), distension and strength of grain (8.9 mm) and shrinkage temperature (>82°C). The results showed that the 'Garad - Neem' blend significantly enhanced the quality of tanned leather to almost double the level of the leather tanned by conventional pure Acacia nilotica pods 'Garad' power.

Keywords: *Leather, Acacia nilotica, azadirachta indica, pretannage, full vegetable tannage, mechanical and physicochemical properties*

1. Introduction

Acacia nilotica is a natural tree that has many uses in Sudan; the pods are used as indigenous tanning materials for full vegetable tanning to produce leather. Simon suggested that the better alternative to chrome tannage is tanning with improved vegetable tanning materials which is environmentally friendly than chromium tannage, cheaper and can easily be applied for various sorts of leather [1]. Hence many attempt to improve the tanning power of indigenous *Acacia nilotica* pods were applied in Sudan particularly pods of the subspecies *nilotica* which has been known and used for tannage since long time ago [2]. In this aspect Musa and Gasm Elseed reported that Sudan has various indigenous tanning materials. Some of these, such as garad pods of *Acacia nilotica subsp. Nilotica* are used extensively in the Sudan by rural tanneries to support characteristic of the tanning materials of *Acacia nilotica* pods [3]. Fagg and James reported that the tannin content of mature 'Garad' pod powder was 23% in Sudanese *Acacia nilotica* [4]. Lamb produced soft leather of very light colour using Garad [5]. Haj Ali & Ahmed performed a comparative study of physical and chemical properties of leathers tanned with spray dried 'Garad' or with spray dried Mimosa and the results showed that usage of Garad powder gave an excellent leather with satisfactory results [6]. Also Mahadi *et al.* studied the chrome free tannage using indigenous materials (Garad powder and aluminum sulphate) and he found that leathers obtained by this method gave high shrinkage temperature (125ºC), elongation at break (65.6 %), tensile strength (38 N/mm^2) and tear strength (98 N/mm) [7]. The problem faced tannage industry is the environmental hazard that had occurred from using chrome tannage. Great efforts were done aboard to modify clean production in tannage industry. Therefore in Sudan there are great opportunities to replace the environmental harmness of chrome by using natural materials. The chemical properties of natural leathers tannage materials were found to be quite normal and eco-friendly processes that reduce the pollution load of tannage and produce high quality leather. The objectives of this study is to improve tannage of leather for shoes by using spray dried powder of natural indigenous materials namely; 80% A*cacia nilotica* pods and 20% *Azadirachta indica* barks; through studying their effects in physico-chemicals properties of shoes leather such as shrinkage temperature, tensile strength and fullness and produced leather with low cost which can replace the imported tanning materials.

2. Materials and methods

2.1 Source of materials

Acacia nilotica pods were brought from Sinnar State, Sudan. Goat pelts were obtained from slaughterhouse of ELKadaro, Khartoum North. Sudan. Chemicals used for the experiment and analysis were of analytical grade.

2.2 Preparation of indigenous tannins material

Spray dried powder was prepared using blending of 80% of *Acacia nilotica* pods powder with 20% of *Azadirachta indica* bark powder. The blended powder was bleached with 5% of *Hibiscus sabdariffa* bark powder and then leached using rotary system then 3% of sodium chloride was aqueous solution added. The leaching was spray dried at inlet temperature of 175°C and outlet temperature of 100°C and 1 atm pressure. The dried sprayed powder was kept in polyethylene bag for further processes.

2.3 Experimental design

The experimental design was outlined in randomized complete design with two treatments; t_1 indigenous method; 100% A*cacia nilotica* pods; and t_2 modified method; 80% A*cacia nilotica* pods and 20% *Azadirachta indica* barks; replicated three times.

2.4 Tanning trails methods

2.4.1 Pretannage

Four pieces of goat pelts; 4kg; were weighed and soaked in experimental drum for 30 minutes with 4 litres of water. The pelts were re-soaked in a pit using 6 litres of water and then left overnight. In the second day the pelts were placed back into the drum and washed for 10 minutes. The hairs were removed by painting unhearing method using a mixture of 80 g of sodium sulphide and 40g of lime in paste formed of 12.6 pH and 20° Be. The pelts were covered with polyethylene and left for 30 hours then scudded manually using scudding knifes and washed in drum for 15 minutes. Then transfer to the drum for reliming with 80g of fresh lime and 4 liters of water and after that washed. Then pelts were replaced into the drum and washed again followed by delimed with 60g of sodium formate and 4 liters of water for one hour followed by drain and washed for 10 minutes. The pH of pelts was adjusted to a pH 8.0 followed by bated at 37 °C for 30 minutes in a drum with 20 g of orboron and 4 liters of water then drained and after that washed for 5 minutes. Four hundred grams of sodium chloride were dissolved in 4 liter of water and then the pelts were run for 30 minutes followed by addition of 40 g of formic acid diluted (1:10) added to the pelts in the experimental drum and run for 40 minutes. The pH was adjusted to 2.5 using formic acid. The pelts remove and covered by polyethylene and horsed up. Thickness of the pelts was adjusted using shaving machine to 0.8 mm.

2.4.2 Tannage

2.4.2.1 Full vegetable tannage

Two pieces; weighing 2.0 kg as dry weight; of deliming pelt were transferred into the experimental drum. Two liters of water and 20g of sodium bicarbonate were added and the pH of pelts adjusted to 5.5. The soaking solution was reduced to 0.8 litres. The pelts were treated with 40 g of sulphonated oil and 125 g of modified; 'garad - neem'; spray- dried powder for 50 minutes. Then the concentration of the bath was raised by adding 125 g of 'garad - neem' spray- dried powder and drumming for 50 minutes. Further 150g of 'garad - neem' powder were added again into the bath and drummed for 40 minutes. Additional 60 g of oil was added and drummed for 50 minutes. The penetration of the tanning materials into the leather was checked by cross section on the leather. Thirty grams of formic acid were added and drummed for 15 minutes then washed and horsed up and covered with polyethylene left over night and toggled. The method was repeated using two pelts; weigh 2 kg and 800 g of crushed 'garad' powder' and the produced leathers were stored to mechanical and physic-chemical tests.

2.5 The mechanical and physico- chemical properties of leather

The samples were prepared according to SLP1&2 then specimens subjected conditioning according to SLP3. Thickness, tensile strength and elongation, tear strength and distension were measured using (SLP 4, 6, 7 and 9)[8] and strength of grain, stitch tearing strength and tong tears strength were measured using (ASTM D.2261 and 4705) [9 and 10]where sampling and physico-chemical properties of leather, moisture, fat, total soluble solid and degree of tannage, were measured using (SLC 1, 2, 3, 4, 5, 6, 7, 9 and 12). [8].

2.6. Statically Analysis

The data analysis of variance performed for comparison was conducted by using a computer program equipped with SPSS statistical analysis method at a significant level $p \leq 0.05$.

3. Results and discussion

3.1 Mechanical and physicochemical properties of produced leathers using improved or indigenous tannins

3.1.1 Thickness

The thickness of the goat leather treated with either indigenous *Acacia nilotica* pods as the control or spray

dried of blending of 20% *Azadirachta indica* and 80% *Acacia nilotica* was shown in Fig (1). The results showed that thickness of leather treated with the modified spray-dried characterized with an excellent cross and fullness compared to the standard of shoe upper leather [11, 12] and it felt in recommended range.

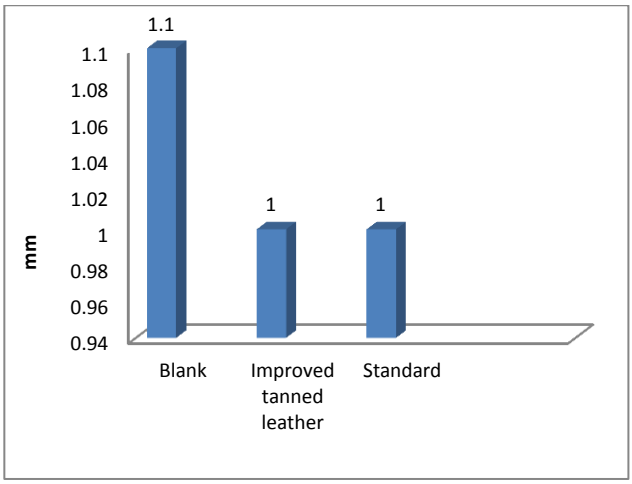

Fig.1 Thickness of vegetable tanned leather

These results suggested that 20% of *Azadirachta indica* change the behavior of tannin and raised tannage power of *Acacia nilotica* by reducing the amount of consumed tannin to half with an increment of leather strength than addition of *Acacia nilotica* only. Because *Acacia nilotica* contains hydrolysable tannin which is better for thickness while *Azadirachta indica* bark contains condensed tannin which impact the strength properties of the tanned leather. Overall collective actions of the power quality of the leather by using 'Garad – Neem' tannage materials increased the homogenous interaction of strength, fullness and fellness that recommended for good leather. These results were agreed with Musa and Gasm elseed whom mentioned that pods of *Acacia nilotica* contain a considerable amount of hydrolysable tannins which undergo hydrolysis in the acid solution. [13] Therefore leathers which were tanned with only conventional 'Garad' are characterized with drawn grain decrease in strength and low shrinkage temperature. Therefore blended *Azadirachta indica* bark rich with condenses tannins [14] controlled the swelling/plumping of yielding leather with thickness closed to standard

3.1.2 Tensile, Tear, and Stitch Tear Strengths

The results of tensile, tear and stitch tear strengths values of the goat leather treated by either *Acacia nilotica* pods or blending ;20% *Azadirachta indica* and 80% *Acacia nilotica*; were shown in Figures (2-4).

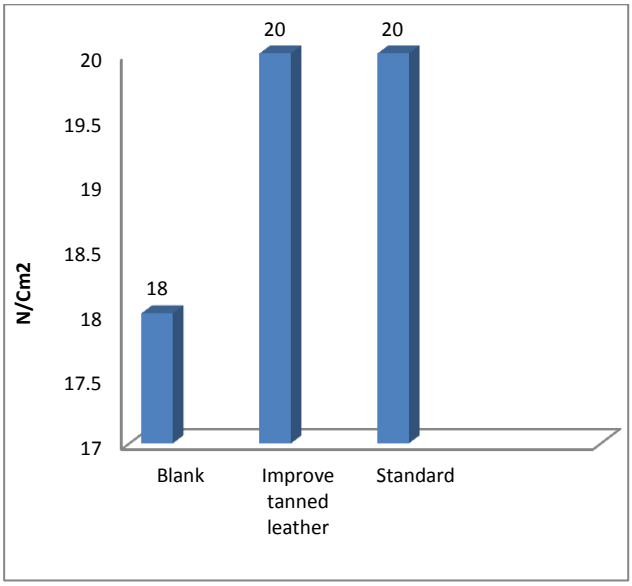

Fig.2: Tensile strength of vegetable tanned leathers

The leathers treated with the blended powder showed better strength in compared with the standard of shoe upper leather which closed in agreement with standard. [11and 12] The strengths values of goat tanned leathers increase by applying a blend of 20% *Azadirachta indica* and 80% *Acacia nilotica*.

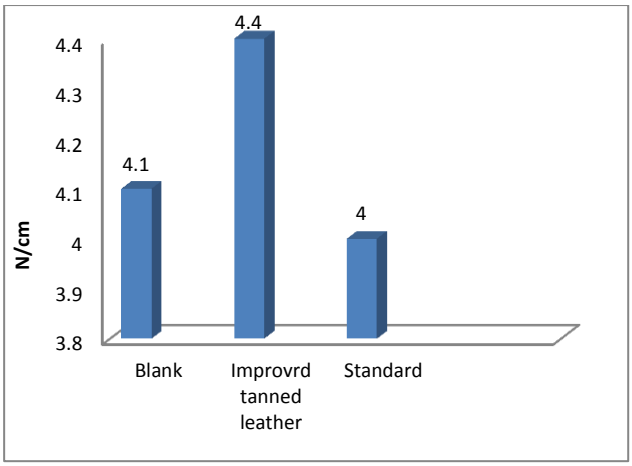

Fig.3: Tear strength of vegetable tanned leather

These results suggested that the presence of 20% of *Azadirachta indica* modifies the tannin conduct and raised the tannage power of *Acacia nilotica* to almost double its normal power. This could be attributed to the existence of considerable amounts of condensed tannins in *Azadirachta indica* bark which seem to be very important to strengthen the leather beside the customary benefits of hydrolysable tannin in *acacia nilotica* required for fullness and color. Orwa *et al*. reported that *Azadirachta indica* bark contains considerable amounts of condensed tannins [15], whereas Lamb found that pods of *Acacia*

nilotica contain hydrolysable types [5]. Therefore, it is quite obvious that the types and contents of tannins together are quite crucial to strengthen the fibres of the leather. Generally collective actions of the power quality of the leather increase with homogenous interaction of strength, fullness and fellness that recommended for good leather. Hence good leather strengths due to the behavior of condensed tannins. Condensed tannins penetrate rapidly and aggregate more readily in the pelt fibres deposited a very large molecules that cross-linking through hydrogen bond to the peptide groups of the collagen.

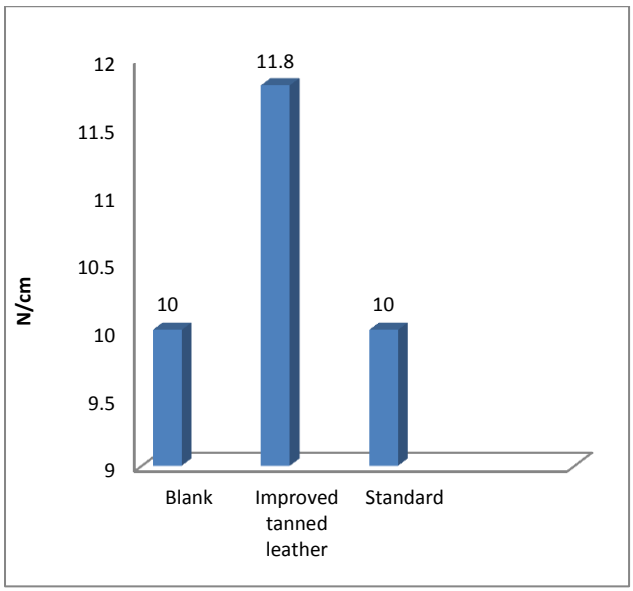

Fig.4: Stitch tear strength of vegetable tanned leather

The degree of cross-linkage depends on the size of the polyphenol molecules and number of –OH groups where hydrolysable type not condensate but hydrolysis deposited sludge with low molecules. Sarkar conception that tannage with condensed tannins was much better than with the hydrolysable tannin and gave the most stable leather [16]. However, extensive and deep studies are needed to investigate the actual role played by each type of tannin species, and the mechanism of the overall tannage process.

3.1.3 Elongation and Distension and Strength of Grain

The elongation and distension and strength of grain of the goat leather tanned using either 100% of *Acacia nilotica* pods as the control or spray dried of blending; 20% *Azadirachta indica* and 80% *Acacia nilotica*; were shown in Figs (5 and 6). The result showed better elasticity, softness and flexibility of blended tanned leather agree with the standard of shoe upper leather [11, 12] and felt in recommended range.

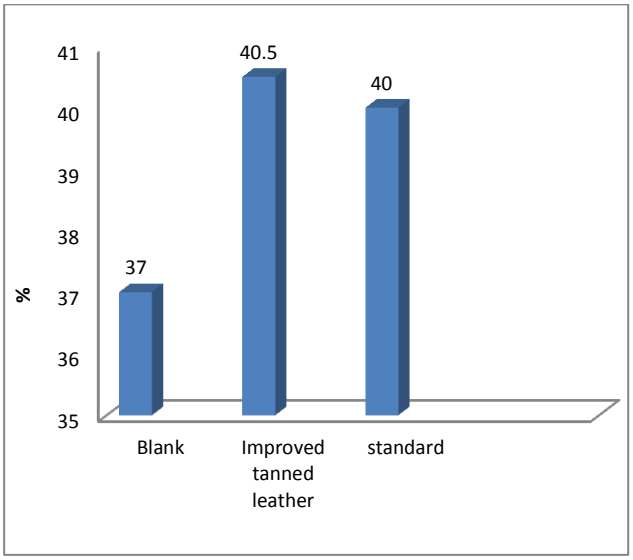

Fig.5: Elongation of vegetable tanned leather

These results postulate that addition of 20% *Azadirachta indica* vary the nature of tannin and raised tannage power of *Acacia nilotica* and reduced consumption of tannin to the half than using *Acacia nilotica* alone. *Acacia nilotica* contain consider amount of hydrolysable tannin which undergo hydrolysis releasing nontannins molecules which reduced the tannin liquor acidity causes an osmotic effect, protein swell and plumps, that accelerates the penetration and fixation of the tannin producing very firm leather.

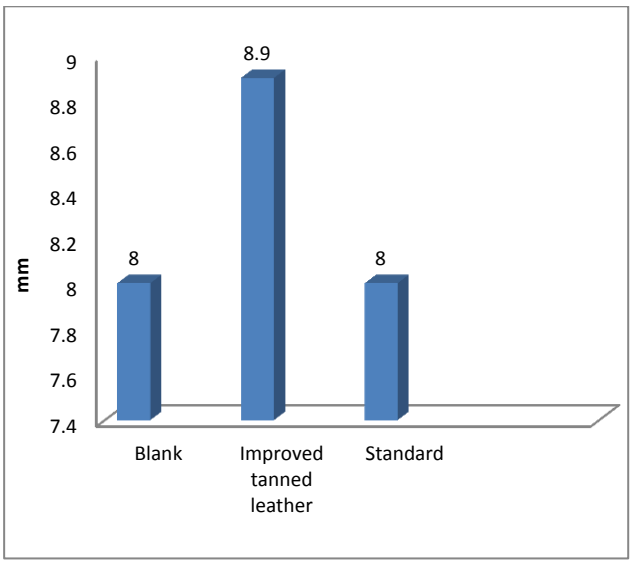

Fig.6: Distension and strength of grain of vegetable tanned leather

Thus it is essential to control the pH of the tanning liquor using blending method, 'Garad – Neem' and natural salt, which organized the protein swelling/ plumping and developed physical properties such as softness, flexibility, strength and thermal stability of yielded leather. This result is coincided with Dutta who mentioned that

increase in acid swelling/ plumping ruptures stabilizing cross-links in the fibre structure, short links, and releases additional hydrogen bond sites, peptides groups, for tannin fixation. Whereas final pH values of 3.6-3.6 produce flexible leather, pH of 3.2 produce very firm leather [17].

3.1.4 Shrinkage temperature

The hydrothermal stability of the goat leathers tanned using either 100% of *Acacia nilotica* pods control or spray dried of blending of 20% *Azadirachta indica* and 80% *Acacia nilotica* were shown in Fig (7). These results proposed that 20% of *Azadirachta indica* modify the tannin nature and increased tannage power of *Acacia nilotica* and reduced amount of consumption tannin to half. *Azadirachta indica* bark wealthy in condensed tannin which acts as strength agent of the tanned leather while *Acacia nilotica* contain high hydrolysable tannin which is reduced thermal stability. Shrinkage temperature assesses the amount of tannin and can enhance the deposition through the cross-section of tanned leather, ended with better elasticity, softness and flexibility of leather.

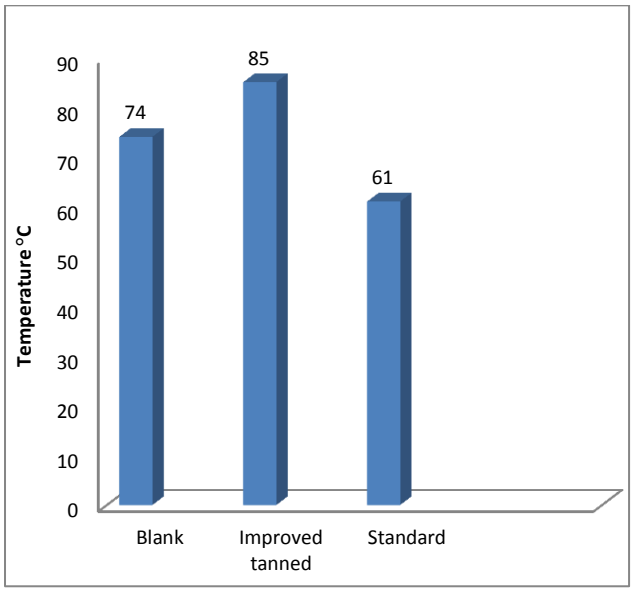

Fig.7: Shrinkge temperature of vegetable tanned leather

The increment of temperature depends on the size of the polyphenol molecules and the numbers of –OH groups which is consistent with Covington *et al*, postulation who concluded that shrinkage temperature is determined by the effectiveness of tanning molecules to produce high molecular weight cross-linked moieties [18]. Also they reported that thermal stability of leather depends on the kinetic stability of the interaction between the tanning molecules and the protein side chains [18]. Larsen *et al*, [19] reported that typical shrinkage temperature for new leather tanned with condensed tannins is 80-85°C while Hydrolysable shrinkage temperature is75-80 °C.

3.1.5 Moisture and Fat Contents

The moisture and free fat content of the goat leather tanned using either 100% of *Acacia nilotica* pods or spray dried blended 20% *Azadirachta indica* and 80% *Acacia nilotica* were shown in Fig (8 and 9). The results showed that elasticity and flexibility of leather agree with the standard of shoe upper leather [11, 12].

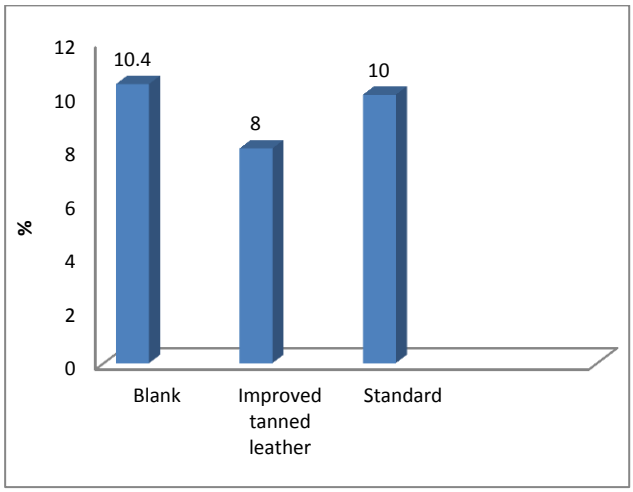

Fig.8: Moisture of vegetable tannend leather

Above mentioned results suggested that both moisture and fat increase the tensile strength and flexibility of leather for a certain limit, firstly, tensile strength is depend on angle of the fibre and their splitting value so low angle and high splitting value yielding high tensile strength.

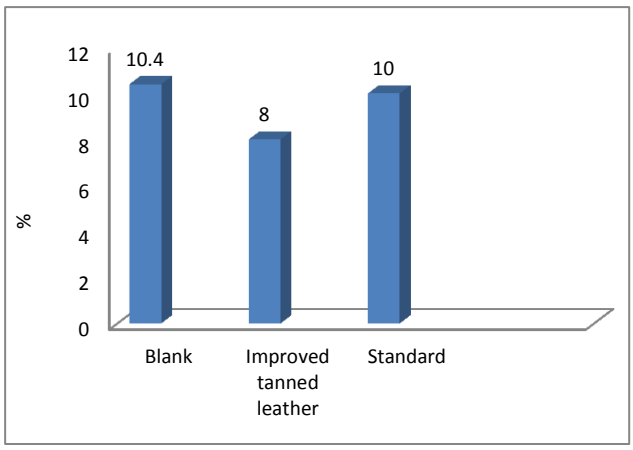

Fig.9: Fat content of vegetable tanned leather

In contrast of that when fibre has lower tensile strength the addition of fat liquor does not lower the fibre bundles angle of weave; but it improve the splitting value of the fiber and its strength. Secondly the leather is flexible when its fibre slid one above the other. The amount of flexibility is estimated using elongation, distension and strength of grain values which indicate if the amounts of moisture and fat content were reasonable

in the fibers or not. This coincided with Hai Quadery who reported that both tensile strength and flexibility changed with the oil content of the leather increased with the increase of its oil content and then decreased after a certain limit. [20] In generally the moisture and fats values present in improved tanned leather are comparable to those of normal standard values.

3.1.6 Total Soluble and Degree of Tannage

Total soluble matter and degree of tannage of the goat leather treated using either 100% of *Acacia nilotica* pods or blended 20% *Azadirachta indica* and 80% *Acacia nilotica* were shown in Figs (10 and 11). The results showed that both total soluble and degree of tannage represented the fixation of tannins on the collagen fibers and the stability of leather.

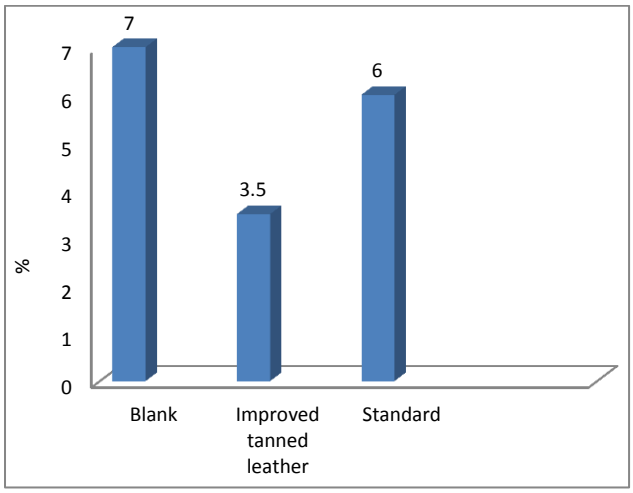

Fig.10: Total soluble matter of vegetable tanned leather

Leather treated with the blended powder showed high stability due to fixation and low soluble matter of condense tannin which agrees with the recommended standard of shoe upper leather [11, 12]. These results suggested that blended 'Garad – Neem' improved the tanning power of indigenous tannin of *Acacia nilotica* and decreased amount of spending tannin to half.

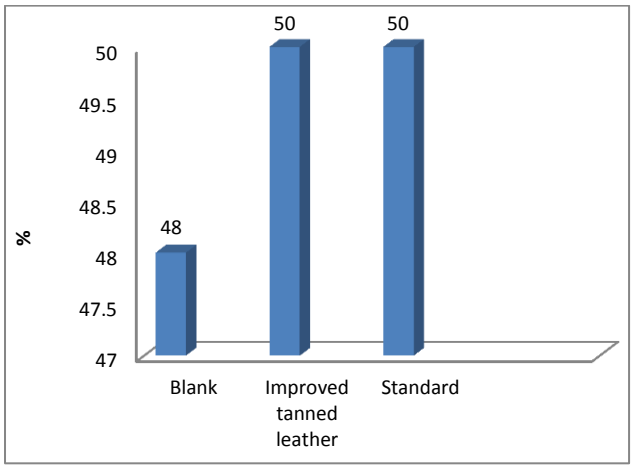

Fig.11: Degree of tannage of vegetable tanned leather

Condensed tannins, 'Neem' is more stable to hydrolysis and microbial attack than indigenous 'Garad' tannins, contain consider amount of hydrolysable tannins, this due to strong co-valent bonding between individual carbon atoms and the absence of ester links. indigenous 'Garad' tannins hydrolysis decomposed the tannin and released sugar and organic acid that increased the soluble matter and decreased the degree of tannage, where condensed tannins are deposit large molecules size of the polyphenol, Reds, contained high numbers of –OH groups which deposit into the pelts fibre and cross-link through large amount of hydrogen bonds to peptide groups in collagen. As reported by Rao, these phenol-peptide strong interactions improve the leather stability [21].

3.2 Statistical Assessment

Table 1 Paired samples of T test for mechanical and physicochemical properties of tanned leathers using either improved or indigenous tannins

No	Description	Mean	Std	Sig. 0.05
1	Thickness mm	1.05	0.07	0.03
2	Tensile strength N/cm^2	19.4	0.72	0.00
3	Elongation %	38.8	1.92	0.00
4	Tear strength N/cm	4.25	0.32	0.00
5	Stitch tear strength N/cm	10.7	0.98	0.00
6	Distension and strength of grain /mm	8.5	0.50	0.00
7	Shrinkage temperature °C	85	4.40	0.00
8	Moisture %	1.05	0.07	0.00
9	Fat %	38.8	1.92	0.00
10	Total soluble matter %	4.25	0.32	0.00
11	Degree of tannage%	10.7	0.98	0.00

Statistical data o f SPSS analysis shows that there are significant differences of mechanical and physicochemical properties of produced leathers using improved tannins comparing indigenous tanned leathers. It should be noted that Table.1 Statistically analysis at $P < 0.05$ level were Gomez and Gomez [22].

Conclusion

Mechanical and physio-chemical characteristics of blended tanned leathers were examined and the results compared to control leathers explained that the experimental process results leathers with good thermal stability and organoleptic properties that is important for commercial viability of the tanning system. Large collective actions of the power quality of the leather increase with homogenous interaction on hydrothermal stability are recommended for good leather. The physical properties of the leathers prepared compiled quite well with the standard requirements. As far as the physical and technical properties of the crust leather concerned; the experimental trial revealed the best performance in terms of softness, fullness, grain stability and general appearance. This sequence, besides the good properties of the final leather is also easily applicable from an industrial point of view.

Recommendations

It is highly recommended that scientific methods must be adopted in harvesting and storage of *Acacia nilotica* pods; because it is seasonal crop contains high tannin concentration that susceptible to microbial damage when harvested and stored in wet climate conditions.

Research's to be conducted to utilize the blended national tanning materials in recommended having eco-friendly tannage with better properties with different plants and concentrations. Phytochemical investigation of tannins in Sudanese plants is recommended.

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