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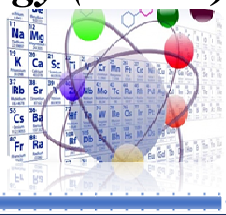

Effect of Different Retanning Agents on Shrinkage Temperature of Leathers

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ABSTRACT

Retanning of tanned leathers played an important role to raise the shrinkage temperature characteristic and quantum of retanning agents, where crosslinks are formed with the polypeptide chain of the collagen or other reactive available sites of the collagen. This study is useful for the tanners to determine the percentage of shrinkage by using different retannages. The results revealed that the maximum thermal stability (increase in shrinkage temperature 21-25%) has been found in the basic chromium sulphate retanned leather without destruction of physical properties. Beside this, other types of retannages i-e, mineral retanning, phenolic based retanning, formalin based syntan have been showed thermal stability upto different levels (increase in shrinkage temperature 4-6%,12-15%, 10-14% respectively) in addition to the development of physical properties such as tensile strength (N/mm^2), tear strength (N/mm), fullness , etc. to suit different needs.

Keywords: Retanning agents, thermal stability, physical testing

1. INTRODUCTION

All raw skins collagen fibers have a definite temperature at which their shrinkage takes place when heated[1]. It is usually 55°C to 65°C of untreated hides & skins[2]. This shrinkage temperature (Ts) is increased due to tanning action where cross linkage of polypeptide chains are formed [3]. Different tanning materials possess different shrinkage effects on collagen tanned leathers obtained from different treatments exhibit different shrinkage temperature[4]. The thermal stability of tanned leather can be increased if it is put to further

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tanning action, usually called retannage, which is nowadays a common practice throughout the world. Leather produced by single tanning agent cannot yield all the desired physical properties. The tanned leather need to retanned for more fullness and improvement in the structure[5]. It has, therefore, become customary among tanners to retanned the leather already tanned, whether it is vegetable or mineral tanned. Raw hides and skins, on treatment with basic chromium sulphate are converted to wet blue leather. These are retanned in different ways according to needs and requirements pertaining to degree of softness, porosity, firmness or flexibility[6].

2. EXPERIMENTAL

2.1. Chemicals, Equipment and Instrumentation

Commercial grade chemicals were purchased from local market without further purification and used in the tannery area. The goat skins without any type of defects were selected for the experimental processing. These were treated in tannery area of Leather Research Centre, PCSIR, *SITE*, Karachi using conventional chrome tanning process while change in the retanning agents was applied. Universal Testing Machine Tinius Olsen model H5KS was used for the physical testing of leather. Leather softness tester (ST 300) was used for softness test. The leathers were tested according to their standard test methods after conditioning. EN ISO 2419, 2006, EN ISO 3377-2, 2002; EN ISO 3376, 2002; EN ISO 17235, 2002;EN ISO2589, 2002. Determination of shrinkage temperature was carried out using STD-114 shrinkage tester from SATRA.

2.2. Research Procedure

Universal Testing Machine Tinius Olsen model H5KS was used for the physical testing of leather. Leather softness tester (ST 300) was used for softness test. The leathers were tested according to their standard test methods after conditioning. EN ISO 2419, 2006, EN ISO 3377-2, 2002; EN ISO 3376, 2002; EN ISO 17235, 2002;EN ISO2589, 2002. Determination of shrinkage temperature was carried out using STD-114 shrinkage tester from SATRA.

2.2.1 Preparation of samples

Four Goat Skins Wet blue shaved at 1.0mm $\pm$ 0.3mm processed at Leather Research Centre for application of each retanning agent as under:

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Table 1. Brief of Tannery Process

Process	Chemical	Duration/Time
Washing	300% Water 35°C	10 minutes
Neutralization	100% Water 0.8% Sodium Bicarbonate 1.0% Sodium Formate	60 minutes pH 6.0-6.5
Draining & Washing	300% Water	10 minute
Retanning	150% Water 50°C Retanning agent at spec.dosage 0.25% Formic Acid	60 minutes 20 minutes pH 4.4
Draining & Washing	200% Water	10 minute
Fatliquoring	200% Water 65°C 1.5% Dye 6% SR Synthetic Fatliquor 7% UPN Fish Oil	45 minutes 60 minutes
	1.5% Formic Acid	30 minutes pH 3.8

The resulted leathers were hanged for overnight then set out and dry at room temperature. All chemicals were applied on the base of shaved weight of each wet blue.

Table 2. Application of retanning Agent on Leathers

Serial number	Type of Retanning agent	%f Retanning agent based on moisture free basis of each wet blue
01	Basic Chromium sulphate	8%
02	Basic Aluminium Sulphate	6%
03	Synthetic Phenolic retanning	6%
04	Formalin based resin (40% HCHO)	6%

3. RESULTS AND DISCUSSION

This study was conducted to determine the thermal stability of collagen fibers of skins on application of different retanning agents as studied earlier of chrome tanned leather[7]. The sample 01 retanned with basic chromium sulphate while other tannery processes were similar in the each skin as presented in Table 1. The maximum increase in shrinkage was occurred in the sample01 when compared to other samples. It has declared that the tanning and retanning both effect on the thermal stability of leather. The strong bonding of

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leather collagen with the chromium co-ordination leads to the inner stability. Leather shrinkage temperature (Ts) is primarily due to the nature of reaction of the tanning materials with different reactive groups of collagen (peptide link CO-NH, carboxyl-COOH-and basic amino-NH_2–group) and number of cross links formed thereby. Some leather chemists are of the opinion that its T_s is due to the interaction between adjacent polypeptide chains[8] which are formed between carboxyl (-COOH) and amino groups (-NH_2) of two different amino acid molecule with the elimination of water, as shown in **Fig. 1**.

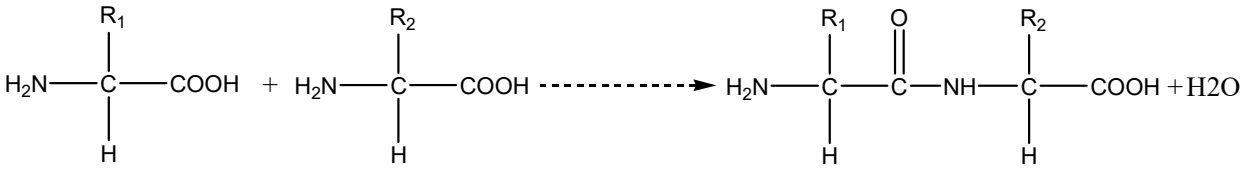

Figure.1. Bond between carboxylic and amino group

It is a molecular phenomenon where protein stabilization takes place in different ways under different condition arising out of treatment with organic, vegetable and mineral tannins. However, according to majority of chemists, protein stabilization takes place by hydrogen bonding when phenolic hydroxyl groups co-ordinate with carbonyl oxygen (-CO-NH) of the peptide links. Retanning of leather fills the looser areas of hides and skins and improves the leather properties such as softness, fullness, grain smoothness, etc. Therefore, all experimental leathers were tested for the various physical parameters as presented in figure 2. The results revealed that the minor differences were found in the leathers after retanned as shown in table 03. The tensile strength (N/ mm^2) was found highest in the chrome tanned and retanned leather. Whereas, the excellent fullness was fund in the sample 4 with stiff grain.

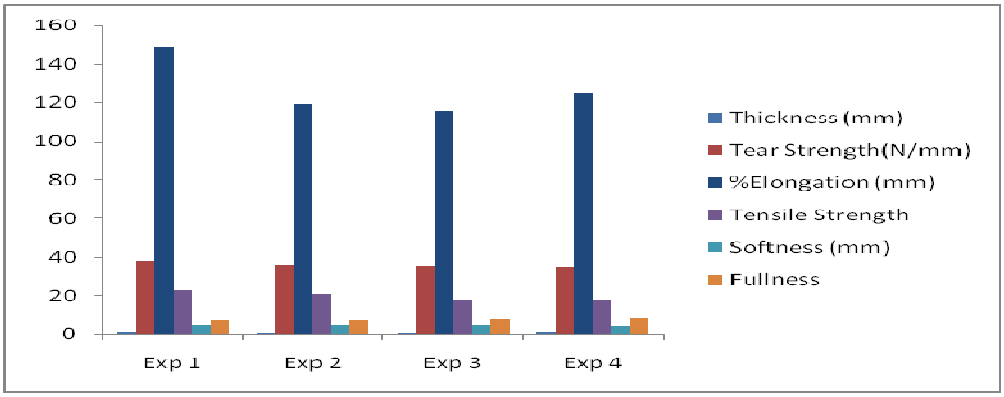

Figure 2. Comparison of physical properties of retanned leathers

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Table 3. Physical characteristics of Retanned Leathers experiments (1-4)

Experiment	Thickness (mm)	Tear Strength (N mm)	%Elongation (mm)	Tensile Strength (N/ mm^2)	Softness (mm)	Fullness	Percentage of increase in Shrinkage temperature (%)	Remarks
Exp 1	1.4± 0.2	37.791 ± 2.50	148.89 ± 1.2	22.550 ± 1.2	5.0 ± 1.0	7 ± 1.0	21-25%	Fullness suitable for case and footwear leather
Exp 2	1.0 ± 0.1	35.70 ± 1.5	119.135 ± 1.6	20.542 ± 1.5	4.4 ± 0.5	7 ± 1.0	4%-6%	Slightly softer feel suitable for upper leather
Exp 3	1.03 ± 0.5	35.341 ± 1.8	115.49 ± 1.0	18.016± 1.0	4.3 ± 1.0	7.5 ± 0.5	12%-15%	Suitable for shoe upper leather
Exp 4	1.35 ± 0.1	34.272 ± 2.1	125.33 ± 0.3	17.244 ± 1.5	4.2 ± 1.0	8 ± 1.0	10%-14%	Fullness with stiff grain suitable for shoe upper, case leather

Note: The all leather samples were conditioned prior to testing. Triplicate
Samples for each test were observed and st.uncertainaty is shown against each test.

This variation may be attributed to the filling action of each retanning agent towards the collage affinity through its chemical sites. The filling action of aldehyde retanning agent is a complicated mechanism. The aldehyde group formed a schiff base by reacting with the amino groups in the collagen[9] . Formaldehyde reacts with amino groups in acidic medium discharging hydrogen from the positively charged amino groups see **Fig. 3**.

Figure. 3.Reaction of formaldehyde

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Many retanning agents based on the cyclic organic such as phenol have used in the tanning and retanning of leather, therefore, the leather retanning was carried out with synthetic phenolic retanning which showed improvement in the leather properties[10].

4. CONCLUSIONS

Retanning of leather plays an important role for thermal behavior stability[11] .The experiments showed that retannage improves not only the thermal stability of leather, but also its physical properties in different degrees. Each retanning agent enhances the porosity of the fiber structure reduces its deformability and density by penetrating into collagen fibers. Tensile strength, compactness or looseness, softness and mellowness, are largely influenced by retannage depending on nature, type and percentage of chemicals used as retanning agents. The chrome retanned leather showed minimum shrinkage as compared to mineral retanned /vegetable retanned leathers. Thus, retannage is an important factor for production of good quality leather to suit the different needs of customers demand starting from footwear and bags to garments and sports goods. Although, this study is very limited moreover, investigations using advanced techniques are needed for further studies.

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