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STUDIES ON EFFECTS OF RETANNAGE ON THERMAL STABILITY OF LEATHER AND ITS USEFULNESS

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Retannage of tanned leather raises the shrinkage temperature (Ts) which is dependent on the characteristics and quantum of tannins used for the purpose, where cross links are formed with the polypeptide chains (-Co-NH-) of collagen or its other reactive groups (COOH-NH_2-). Vegetable tanned leather of 75° Ts when treated with organic, synthetic and mineral tanning agent gave Ts rise of 15 °, 16° and 35° respectively. Full chrome tanned leather at 105° Ts when treated with organic, synthetic and mineral tanning agent gave Ts. rise of 14°, 20° and 25° respectively in varied proportion in addition to the development of physical properties to suit different needs.

Key words: Retannage, Thermal stability, Leather.

Introduction

Thermal stability of collagen fibres of hides and skins is one of the criteria of determining whether it is tanned or untanned. All raw collagen fibres have a definite temperature at which their contraction takes place. It is usually 55° to 65° [1]. This shrinkage temperature (Ts) is increased due to tanning action where cross linkage of polypeptide chains are formed. Different tanning materials have different effects on collagen. Tanned leathers obtained from different treatments exhibit different shrinkage temperature. The thermal stability of tanned leather can be increased if it is put to further tanning action, usually called retannage, which is now-a-days a common practice throughout the world. Leather produced by a single tanning material system can not yield all the desired physical properties. It has, therefore, become customery among tanners to retain the leather already tanned, whether it is vegetable or mineral tanned. Raw hides and skins, on treatment with basic chrome 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.

Materials and Methods

Goat and calf skins were taken as raw materials for the experimental work. In the delimed or pickled condition these skins were put into vegetable or chrome tanning systems resulting in Ts 75 and 100° respectively. These were taken as the standard materials which were subjected to a system of retannage with different tanning chemicals, mineral organic synthetic or phenolic.

These include chromium sulphate of 33% and 48% basicity formaldehyde (48%), synthetic tannins, mimosa and babul bark extract. Tanning was carried out on delimed or pickled pelt using different tanning materials separately to determine the normal thermal stability of leather for comparison.

For the purpose of tanning of the tanned leather, conventional methods of retannage or combination tannage were adopted and thermal condition was recorded in each case. The best method as recorded was the retanning of chrome tanned leather with resinous syntan which increases the shrinkage temperature of the tanned leather from 100° to120°. Retanning with phenolic syntan also increases the shrinkage temperature of the tanned leather from 100° to 116°.

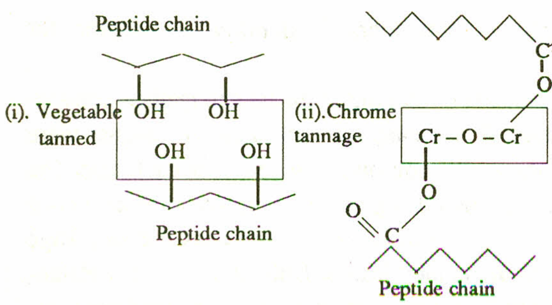
Results and Discussion

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 Ts is due to the interaction between adjacent polypeptide chains, which are formed between carboxyl (-COOH) and a amino groups (NH_2) of two different amino acid molecule with the elimination of water, for example:

$$\mathrm{NH_2{-}\overset{R_1}{\underset{H}{C}}{-}COOH + NH_2{-}\overset{R_2}{\underset{H}{C}}{-}COOH \rightarrow -NH_2{-}\overset{H}{\underset{R_1}{C}}{-}CO{-}NH{-}\overset{H}{\underset{R_2}{C}}{-}COOH + H_2O}$$

It is actually a molecular phenomena where protein stabilization takes place in different ways under different condition arising out of treatment with organic, vegetable and mineral tannins. Due to the inadequate knowledge of chemistry of vegetable tannins, the exact mechanism of reaction between collagen and tannins has not yet been established. However, according to majority of chemists, protein stabilization takes place by hydrogen bonding when phenolic hydroxy groups co-ordinate with carbonyl oxygen (-Co-NH) of the peptide links [2] although it was suggested by Knapp [3] a century ago that it was more physical deposition of tannins on collagenous fibres.

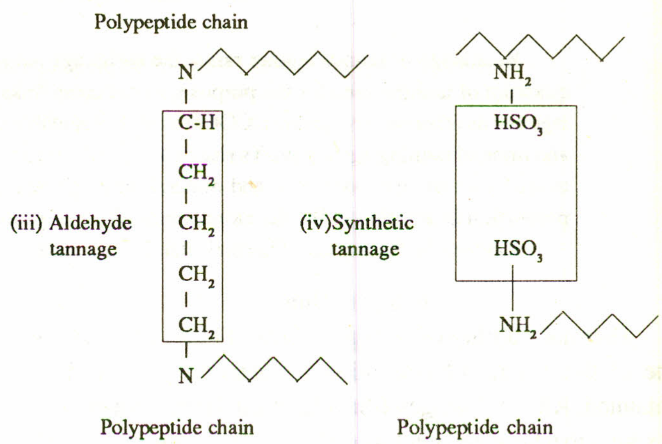
White's observation indicate that all the three functional groups of protein take part in hydrogen bonding, according to the type of amino acids and pH condition [4]. It is believed that all of the known functional groups in vegetable tannins participate in these reations. It is probable that cross linking is effected by secondary valence through hydrogen bridges with the (-OH) groups of the phenolic tanning agents. In mineral tannages, cross linking is effected by the principal valence through co-ordinate bond with carboxyl (-COOH) groups of collagen [5]. This can schematically be represented as follows:



In formaldehyde tannage, amino groups of collagen are actively involved in the reaction raising the shrinkage temperature of collagen. Here HCHO reacts with amino groups in acid medium discharging hydrogen from the positively charged amino groups [6,7].

$$R - NH_3^+ + HCHO ...... R\text{-}NH\text{-}CH_2OH + H^+$$

Here, in this aldehyde tanning system glutaraldehyde, e.g , forms cross link by principal valency via atomic bond, while in synthetic tanning operation, no cross linkage but secondary valence linkage is formed by electro valent salt bridge, that is, ionic bond of the HSO_3^- with $-NH_2$-groups of collagen [8].



In this way, shrinkage temperature of collagen is raised on tanning with different chemicals used separately in varied proportions as the main tanning agent (Table 1).

A close examination of the results in the Table 1, indicates that shrinkage temperature has risen in each case. It is the highest when chrome compound was used (112°). In case of vegetable and aluminium tannage, Ts was of the lower range (70°- 80°).

Table 1. Thermal Condition (Ts) Pickled Pelt After Treatment With Formaline Chrome and Vegetable (Mimosa) Tans Compound.

S. No.	Type of the tanning compound used	Amount used on pelt Wt. %	Shrinkage temperature (°C)	Remarks
1.	(a) Basic chromium sulphate	5	90 – 93°	Under tanned
	(b) " "	6	95 – 97°	"
	(c) " "	7	99 – 100°	Tanned
	(d) " "	8	100 – 102°	Full tanning
	(e) " "	10	108 – 112°	"
2.	(a) Basic aluminium sulphate	6	70 – 72°	Under tanned
	(b) " "	12	78 – 80°	"
3.	(a) Formalin (40% HCHO)	4	80 – 82°	Tanned
	(b) " "	6	82 – 84°	"
	(c) " "	8	82 – 84°	"
4.	(a) Mimosa extract	20	70°	Inadequate tanning
	(b) " "	30	76 – 80°	Tanned, suitable for lining leather
	(c) " "	35	80 – 84°	Tanned, suitable for sole leather
	(d) " "	40	80 – 84°	" "

Now, these tanned leather is put to further tanning action using basic chromium or aluminium sulphate, and aldehyde, vegetable as well as synthetic tannins as retanning agents with the consequence of rise in shrinkage temperature in different degrees. In the first case, chrome tanned leather at 100° was used (Table 2).

It is evident from the Table that 4% basic chrome when used for retanning of chrome tanned calf leather at 100° gave a Ts rise to the extent of 14°. It was further raised when 6% basic chrome was used. Ts rise was poor (only 4°-6°) in case of basic aluminium sulphate. Use of 6% phenolic syntan gave 12°-15° rise in Ts. while it was higher in case of resinous synthan. 6% formalin (HCHO) gave a Ts. rise by 10-14° Ts. rise is low in case of vegetable tannin. Use of 15% mimosa extract gave only 6°-10° rise in Ts.

In the second case, vegetable tanned leather having Ts. 75° obtained by subjecting the delimed pelt to the action of blended mimosa and babul bark extract, was used to asses the condition of retanning with several tanning agents. This leather when treated with basic chrome and aluminium sulphate, aldehyde and syntan, there was a considerable rise in Ts. ranging from 4°-35° under different conditions (Table3).

Analysis of the results indicate that goat skin pelt when tanned with babul bark extract blended with mimosa, has its Ts. 75°. This leather on retanning with 6% basic chromium sulphate has got its Ts. enhanced to 97° showing an increase of 22°. Further addition of 2% basic chrome salt, enhanced the Ts. by 13° more. Under similar conditions of using basic aluminium sulphate, as a retanning agent, Ts. rise was only 4°-6°. In case of 6% aldehyde, the enhancement was by 15°. Better results were, however, obtained when resinous syntan was used. Ts. rise was to the extent of 16° while it was only 8° when phenol-based syntan was used.

Explanation. The reasons of rise in shrinkage temperature for retanning of tanned leather, can broadly be attributed to the formation of cross links between active groups of the tanning materials as already mentioned, and untreated functional groups in the collagen, or there may be co-ordination condensation polymerization and formation of complex compound. According to Gustavson and Theis [9,10] vegetable tanned leather, for example, when treated with formaldhyde, there may be additional cross links formed of HCHO with the untreated reactive groups in the collagon, or aldehyde condensation takes place with vegetable tanning.

About chrome-aldehyde retannage, Theis and Kloppinger [11] are of the opinion that aldehyde reacts with activated basic groups of collagen or there is a co-ordination of aldehyde with chrome complex . This supports the earlier view of Gustavson [12].

It has also been observed that rise in shrinkage temperature in chrome-vegetable and vegetable-chrome retanning system, depends on chrome content, basicity and stripping of vegetable tans.[13-16].

Benefits. Retanning is practically a gurantor of full tanning of hides and skin. It saves the leather from deterioration, in case it has been left undertanned inadvertently during the main tanning process.

Practical experiments show that retannage improves not only the thermal stability of leather, but also its physical properties in different degrees [17]. It enhances the porosity of the fibre structure, reduces its deformability and density by isolating the fibres. Area and thinkness are also increased it

TABLE 2. THERMAL CONDITION (TS) INCREASE DUE TO RETANNAGE OF CHROME TANNED CALF LEATHER.

S. No.	Ts of full chrome tanned leather 100° (33% basic chrome		Material and its quantum used as a retanning agent %on shaved wt.	Final Ts. °C	Increase in Ts. °C	Remarks
1.	"	"	Chromium sulphate (Basicity 48%) 4	112 – 114°	12 – 14°	Compactness with mellowness. Good corrected grain upper leather.
2.	"	"	Chromium sulphate 6	121 – 125°	21 – 25°	" "
3.	"	"	Basic aluminium sulphate 6	104 – 106°	4 – 6°	Fulness and compactness achieved.
4.	"	"	Formalin 6	110 – 114°	10 – 14°	Slightly firm, may be used for upper leather.
5.	"	"	Phenolic syntan 6 (Basyntan – DLX)	112 – 115°	12 – 15°	Medium soft with flexibility can suitably be used as industrial glove, apron and upholstery leather.
6.	"	"	Resinous syntan 6 (Retingan - R7)	116 – 120°	16 – 20°	Fulness and medium softness suitable for footwear.
7.	"	"	Vegetable tanning extract 15	106 – 110°	6 – 10°	Reasonably soft, can be used as shoe-upper and case leather.

Tabel 3. (Ts) Increase Due to Retannage of Vegetable Tanned Leather.

S. No.	Ts of blended vegetable tanned leather (°C)	Material and its quantum used as a retanning agent % on air dye weight	Final Ts. (°C)	Increase in Ts. (°C)	Remarks
1.	75°	Basic chromium sulphate 6% (chromosol).	97°	22°	Fullness suitable for case and footwear leather.
2.	75°	Basic chromium sulphate 8% (chromosol).	110°	35°	"
3.	75°	Basic aluminium sulphate 6%.	79°	4°	Slightly softer feel suitable for upper leather.
4.	75°	Basic aluminium sulphate 12%.	81°	6°	"
5.	75°	Aldehyde (HCHO) – 6%.	90°	15°	Fullness with stiff grain suitable for shoe upper, case leather.
6.	75°	Synthetic tannin - phenolic based DLX – 6%.	83°	8°	Suitable for shoe upper leather.
7.	75°	Resinous syntan 6% Retingan R7.	71°	16°	Selective filling action, tight grain good for embossed leather for value added goods.

also increases the fat retention property of leather. Tensile strength, compactness or loseness softness and mellowness, water affinity or water repellency are largely influenced by retannage dependings on nature, type and quantum of chemicals used as retanning agents.

So, retannnage is an important factor for production of good quality leather to suit the different needs of man in his day-today life, starting from footwear and bags to garments and sports goods.

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