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EFFECTS OF RETANNING FOR BETTER UTILISATION OF LOW GRADE SHEEPSKINS

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Generally 20-25% of all available skins are of poor hide-substance. Investigations were made to convert the inferior skins into quality leather of high Ts with considerable tensile and bursting strength rendering them fit for case, wallet and glove leather. Two different processes were followed. The first process comprises polymerisation-tannage followed by chrome retannage. The second process is based on the principle of retanning of combination tanned leather. The products in each case were compared with their corresponding (chrome tanned) sides of the same skins. In the first case, thickness of the product was seen to increase by 50% with diminished surface having Ts between 98-110^{o}.Weight-gains, of course, were not above 25%. In the second case, Ts of the product ranged from 115-128^{o} with weight-gains and thickness-increase by 60% and 63% respectively when compared to straight chrome tanned sides of about 3.5% chronic oxide content. Tensile and bursting strength were nominally less than that of the straight chrome tanned sides.

INTRODUCTION

Hides and skins are the chief basic raw materials of leather industry. Pakistan produces about 39 million hides and skins of which 34 millions come from goats and sheep. Unfortunately, about 25% of all the available skins are of poor hide-substance. Normally, 25 to 30% of all hides and skins belong to the category A' (first grade), 30 to 50% to the category B and the rest fall under the category C or rejections. These rejections are practically of the poor hide-substance. In these skins, the dermal layer which contains both fibrous and non-fibrous proteins is not fully developed due to malnutrition, disease, and other allied causes.

The fibrous protein, better known as collagen fibre, practically yields leather on tanning. The nitrogen content of goat and sheep skins is slightly more or less than 18%. [1] Empty leathers which are produced from low grade skins are partially lacking in what is called leather producing material (hide-substance).

The most profitable use of the skin lies in the production of shoe-supper leather, garments, gloves, etc. But, these low grade skins are generally used as cheap lining materials in footwear (as mid-soles/in-soles), bags and suitcases and fetch less return. If these could be improved and utilised for shoe-upper, glove, garment, fancy bags and articles, it will bring economic gains.

Investigations were made to produce quality leather out of low grade sheep skins. The results show that the leather thus produced could be used for the production of fancy bags, gloves, and other articles, as the quality of leather pertaining to its thickness, weight and shrinkage temperature, has been enhanced, maintaining the tensile strength, elasticity and bursting strength within reasonable limits.

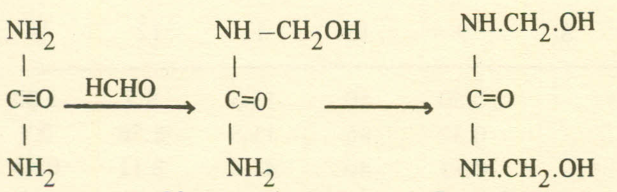
Thickness of leather is an important factor. Sometimes its thickness is less than 0.8 mm when the leather is produced from inferior skins even by adopting the process of chrome tanning. But the normal requirements for gloves, garments and footwear are in the order of 0.8, 1.0 and 1.25 to 1.8 mm. respectively.

Thermal stability of leather fibres is of paramount importance for the durability of leather. Articles made of leather in the country cannot stand higher temperature. The shrinkage temperature of garment and glove is around 100^{o}. If its Ts can be raised to 120^{o} (maintaining the cost of production within the limit), its life will be of higher duration. A good shoe-upper leather, apart from being a thermal insulant, must be strong, soft, pliable, reasonably water-resistant but permeable to water vapour, besides its shape-retaining property.

EXPERIMENTAL

Two different tanning techniques were adopted. In the first case the process of polymerisation tannage *in situ* was followed. [2] The second technique was based on the principles of combination tannage. [3]

Polymerisation tannage. The delimed pelt of one sheep skin was longtitudinally cut into two halves from the middle. The left half of the pelt was treated with 7% *Chromosol* B (chrome tanning powder containing 26% Cr_2O_3) on the weights of the pelt. The other half was put to the action of 10% urea (on pelt weight) followed by the addition of the required quantity of formaldehyde for the formation of dimethylol urea by condensation [4]. These methylol (di) compounds are thought to polymerise *in situ* through interaction between the hydroxyl and amino groups with the elimination of water [5].



Urea   Mono methylol urea   Dimethylol urea.

It was then retanned with 4 and 6% chrome tanning powder (*Chromosol* B) separately and finally treated with 6% fat liquor. The physical properties attained by the product are given in the Table 1.

Combination tannage. Two halves of one sheepskin were treated with basic chromium sulphate so that their chromic oxide content is around 3.5%. As a matter of fact 6% *Chromosol* B on the weights of limed pelt was used. The left side, after basification and neutralisation, was put to fat-liquoring with 6% sulphonated oil. The right half of the chrome tanned leather was treated with 3% synthetic taninous compound, followed by vegetable tannage with 18% mimosa extract. Experiment was also performed with the extract of babul bark which contains 12% tannin [6] This combination tanned leather was retanned with 2,3,9, and 12% of phenolic syntan.[7] The experiment was repeated several times and finally the leather was treated with the sulphonated oil as before. Results are tabulated in Table 2.

Tanning experiments with dimethylol urea *in situ* show that the substance of the inferior skins is considerably increased. Weight-gains by leather vary from 15 to 25% and consequently its thickness increased from 30 to 60% when compared to the product from straight chrome tannage.[8]

Thermal stability is an important factor. Though the substance is increased, the shrinkage temperature remains very low. After polymerisation tannage the Ts was observed to be 78°. On further treatment with 4% *Chromosol* B the Ts rose upto 98-99°. Ts was further enhanced when it was treated with 6% *Chromosol* B. Table 1 shows that Ts may rise up to 110° if treated with 6% chrome on weights of the pelt. The grain surface of leather thus produced was not rough. The degree of softness of leather will depend upon the quantity and nature of fat liquor.

Table 1. Some important physico-chemical properties acquired by chrome retanned polymerised crust leather and its comparison with the corresponding chrome tanned sides

Sample No.	Side	Material used in the tanning process	Shrinkage temparature in °C	In comparison to sample chrome tanned crust leather			Tensile characteristics		SATRA Grain crack		
				Weight gains %	Average thickness increase %	Surface shrinkage (%)	Tensile strength in kg per mm^2	Elongation (%)	Bursting load in kg. per mm thickness	Distension at break in mm.	Bursting strength $K = \frac{P}{D\text{-}a}$
1.	a-Left	*Chromosol B* 7%	100	–	–	–	1.5	30	32	10.7	5.45
	b-Right.	Di-methylol urea *Chromosol* = 4%	98.5	22	45	30	0.8	35	27	9.45	4.60
2.	a-Left.	*Chromosol* 7%	100	–	–	–	1.33	40	20	8.45	3.41
	b-Right.	Di-methylol urea *Chromosol* – 4%	98	20	48	20	.86	45	15	7.3	1.27
3.	a-Left.	*Chromosol* 7%	100	6	–	–	1.07	45	23.2	8.05	3.95
	b-Right.	Di-methylol urea Chromosol – 4%	99.5	15	30	15	1.0	45	21.5	8.70	3.66
4.	a-Left.	Chrome - 7%	100	–	–	–	1.6	35	40	11.0	6.81
	b-Right	Di-methylol urea *Chromosol* – 6%	107	20	50	18	1.2	40	43	10.0	5.62
5.	a-Left	*Chromosol* 7%	100	–	–	–	1.4	45	36	9.5	6.13
	b-Right.	Di-methylol urea *Chromosol* – 6%	110	25	50	Negligible	1.1	42	33	9.0	5.11

Table 2. Some important properties effected by retanning of combination tanned leather and its comparison with simple chrome tanned sheepskins

Sample No.		Type of tannage		Shrinkage temperature	Compared to simple chrome tanned side			Tensile characteristics		SATRA grain crack		
	Side	Simple chrome tannage with 6% chromosol B.	Retanning of combination leather phenolic syntan	TS (^oC)	Weight gains %	Average thickness increase %	Surface shrin-	Tensile strength in kg per mm^2	Elongation %	Bursting loading kg. per mm thickness	Distension at break in mm	Bursting strength $K=\frac{P}{D-a}$
1	2	3	4	5	6	7	8	9	10	11	12	13
1.	a-Left	Chrome only	–	97	–	–	–	0.50	50	13.5	9.5	1.00
	b-Right	Chrome	2	112	38	48		0.32	45	11.8	8.56	0.9
2.	a-Left	Chrome only	–	97	–	–	–	0.83	40	41.6	8.11	0.45
	b-Right	Chrome	2	112	47	40		0.66	25	31.25	7.15	0.28
3.	a-Left	Chrome only	–	97	–	–	–	1.4	65	33.6	10.21	0.45
	b-Right	Chrome	3	118	55	65		0.82	40	20.0	8.55	0.42
4.	a-Left	Chrome only	–	97	–	–	–	1.2	49	18.3	11.1	0.59
	b-Right	Chrome	3	118	55	60		0.92	44	16.22	10.85	0.54
5.	a-Left	Chrome only	–	97	-	–	–	1.24	50	14.55	7.8	0.71
	b-Right	Chrome	6	122	55	48		0.74	38	9.4	8.05	0.67
6.	a-Left	Chrome only	–	97	–	–	–	0.85	55	20.0	10.2	0.68
	b-Right	Chrome	6	122	58	62		0.60	40	18.0	7.24	0.51
7.	a-Left	Chrome only	–	97	–	–	–	1.55	60	18.0	13.7	1.1
	b-Right	Chrome	9	122-125	60	50	–	0.66	40	10	9.5	0.958
8.	a-Left	Chrome only	–	100	–	–	–	1.49	65	20	14.8	1.12
	b-Right	Chrome	12	122-125	55	62		0.65	42	12	10.2	0.91

N.B.: Combination tannage includes treatment with 3% synthetic tanning and 18% mimosa extract on shaved weight of chrome tanned leather.

Retanning of chrome tanned leather lowers its tensile as well as bursting strength. If, however, 6% *Chromosol* B is used for retanning of polymerisation tanned leather, fall of tensile strength/bursting strength is nominal, compared to straight chrome tanned leather.

Retannage of combination tanned leather. When tanned leather is retanned with another tanning material the process is termed combination tannage. Combination tannage raises the shrinkage temperature of leather which is very important, as shrink-test is actually a means of determining leatherity. Bows and Hobb reported that basic chrome can raise Ts upto 100^o. Retanning with vegetable will enhance Ts and render it resistant to wet heat and dry heat [9,10]. It was observed during the experiment that the condition is further improved if it is treated with a low percentage of anionic synthetic tanin. In full chrome tanned leather when treated with 2% of it followed by 18% mimosa extract, an increase of Ts by 12^o was noted. Use of 10% vegetable tannin will also give satisfactory results. Ts difference by 3^o to 5^o was observed.

Keeping all these in view, combination tannage was effected with three different tanning materials (chrome 6%, anionic synthetic tannin 3% and mimosa 18%). It was then followed by retanning with phenolic syntan in different proportions. Table 2 indicates that Ts can rise above 122^o. But an excess of syntan will weaken the leather. Addition of more than 6% syntan in this case is useless. It is evident from the Table that excess syntan reduces the tensile strength and bursting strength of leather. Satisfactory results were obtained by using 3%

Table 3. Shrinkage temperatures under different conditions of tanning and retanning goatskins and properties developed

S. No.	Simple chrome tanning with chromosol 'B' (%)	Combination tannage blended vegetable tanning	Retanning with certain phenolic syntans (%)	Shrinkage temperature (TS) ^oC	Thickness increase % in comparison chrome tanned sides	Condition of grain surface	Remarks
1	2	3	4	5	6	7	8
1.							
(a)	5	–	–	93	–	–	–
(b)	5	T1-5	2	107	10-12)	Soft and	Suitable for both
(c)	5	T1-10	2	110	10-12)	smooth grain.	case and wallet
(d)	5	T1-15	3	114	20	Smooth grain.	Good for footwear
(e)	5	T1-20	3	117	25-28	A bit rough	Suitable for hair cell shoe-upper, reptile imitation leather by embossing
2.							
(a)	6	–	–	97	–	–	–
(b)	6	T1-5	3	115	15-18	Smooth no	For wallet.
(c)	6	T1-15	3	118-120	25	cracking, A bit rough, no cracking.	Case and footwear leather.
(d)	6	T2-15	3	125	30-32	- do -	–
(e)	6	T2-20	3	128	30-32	- do -	–
3.							
(a)	7	–	–	100	–	–	–
(b)	7	T2-10	3	123	35-37	No cracking.	Good for case and footwear
(c)	7	T2-15	3	128	40	–	–
(d)	7	T2-20	4	132	45-47	Stiff and a bit)	Suitable for embos-
(e)	7	T2-20	5	135-136	50	harsh.)	sed finish leather for footwear and port-folios.

N.B. T1 contains 85% mimosa and 15% myrabalan, to which is added a particular synthetic tannin 2% on shaved weight while in T_2 it is 3%

phenolic syntan when Ts was 118^o. Tensile strength and bursting strength were also not so low. Similar treatment of goatskins in place of sheep skins, shows further enhancement of shrinkage temperature. Table 3.

During this process of retannage, the thickness of the leather was found to increase by 25% above what is obtained by straight chrome tannage. Fullness of the leather may be due to the presence of particulate matter in the inter-fibrillary space of leather. The suppleness of leather is due to tannins deposited on tannins.

Burton, Reed and Wood who exemined chrome, zirconium and vegetable tanned leather, support this views [12,13]. The product is distinguishable from other tanned leather by its suppleness. Though pyrogallol produces water resistant leather with chrome, catechol (mimosa) was taken in all cases only from the considera-tion that it exerts more influence on thermal stabilities of leather than pyrogallol tannins [14,15,16,17].

RESULTS AND DISCUSSION

Retanning of combination tanned leather is most suitable for soft shoe-upper, case, garment and wallet leather. The process is slightly costlier than the process of polymerisation (urea-formaldehyde) tannage. But this process has its advantages over other usual processes of tannage in this sense that it can stand higher temperature and can be used as label leather for jeans and garments as well. Iron will not stain it even in wet conditions. It can easily be put to both pigment finish without dyeing. Besides, a certain product of this tanning process can be finished as biscuit coloured leather for fancy bags without the use of dyes and pigments, if mimosa is blended with myrobalan in a suitable proportion.

Leather made by polymerisation tannage with 6% chrome can be used as tight grain upper leather and case leather.

Further, the grain-damaged skins can satisfactorily be converted into washable chamois-type soft leather for jackets and gasoline-filtration for aircraft [18]. Lamb-skins come under the category of skins of poor-hide substance. By adopting the process of combination tannage for white leather, it can be converted into fancy fur leather with increase in weights and substances. Embossed finish goat leather can be used for value goods.

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