(REFEREED RESEARCH)

DETERMINATION OF THE EFFECTS OF SPLITTING AND SHAVING OPERATIONS BEFORE TANNING AT SHOE UPPER LEATHERS ON THE QUALITY OF LEATHER

AYAKKABI YÜZLÜK DERİLERDE TABAKLAMA ÖNCESİ YARMA VEYA TIRAŞ İŞLEMLERİNİN DERİ KALİTESİNE ETKİLERİNİN BELİRLENMESİ

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Received: 13.11.2015 Accepted: 18.12.2015

ABSTRACT

In this study, the effects of splitting and shaving process before tanning on the quality of leather are investigated. Within this scope, leathers are processed as shoe upper by splitting after liming and shaving after pickling methods and then by tanning as chrome, vegetable and wet-white. It is statically examined whether there is a significant difference between the physical and chemical properties of the leathers according to the tanning method used in this study. As a result, the quality properties that are examined, have been found to be generally high on the leathers that are processed by splitting and shaving before tanning compared to traditional methods.

Keywords: Leather, Tanning, Liming, Splitting, Pickling, Shaving.

ÖZET

Bu çalışmada; tabaklama öncesi yarma veya tıraş işlemlerinin deri kalitesine etkileri araştırılmıştır. Araştırmada deriler, kireçlikten yarma ve pikleden tıraş yöntemleri ile krom, bitkisel ve wet-white tabaklanarak ayakkabı yüzlük işlenmiştir. Kullanılan tabaklama yöntemine göre derilerin fiziksel ve kimyasal özellikleri arasında anlamlı bir farkın olup olmadığı istatistiksel incelenmiştir. Sonuç olarak, incelenen kalite özelliklerinin tabaklama öncesi yarma veya tıraş işlemi yapılan derilerde geleneksel yönteme göre genellikle yüksek olduğu görülmüştür.

Anahtar Kelimeler: Deri, Tabaklama, Kireçlik, Yarma, Pikle, Tıraş.

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1. INTRODUCTION

Man and his early ancestors have exploited the unique properties of skin and leather for millennia and almost all human cultures have developed specialist techniques to utilize this readily available raw material for a wide variety of purposes. Indeed, tanning has been described as man's first manufacturing process (1).

Leather production involves a complex sequence of chemical reactions and mechanical processes. Amongst these, tanning is the most important stage giving the hide or skin the required stability. Preserving them from decay by tanning pre-and after-treatment generates a final product with specific properties; stability, appearance, water and abrasion resistance, temperature resistance, elasticity and permeability for perspiration, air, etc (2).

The purpose of unhairing-liming is to remove the hair and epidermis. The hides are treated with 3% sodium sulfide containing 25% sulfide and 3% hydrated lime (calcium hydroxide) in a 200% float (a solution consisting of 2 l of water per kg of skins or hides processed). The sulfide pulps the hair and the epidermis, the lime is used as a buffer to keep the pH at about 13, which causes the hides to swell, the collagen fiber network to open, and which helps the removal of the nonstructural proteins (3).

When the hides or skins are plump in the limed state, this may be an appropriate stage to split them into two or more layers, i.e. a grain layer and one or more flesh layers. This may be desirable because the natural skin varies in thickness, e.g. the neck of calfskins may be twice as thick as the rest of the skin (4). Splitting limed hides can be considered a cleaner technology since it saves chromium and other chemicals (5).

The purpose of pickling is to acidify the pelts to a certain pH before chrome tannage and thus to reduce the astringency of the chrome tanning agents (6).

The differences of thickness at the different sides of the leather are reduced to minimal degree by shaving process and the leather is carried to the demanded thickness. The more the splitting machine works sensitive, the more the shaving treatment gets easy and at that point, a homogeneous thickness is obtained (7).

This study was applied to investigate how splitting and shaving treatments before tanning change some physical and chemical properties of bovine leathers compared to the traditional methods. For this purpose the tanned leathers (chrome, vegetable and wet-white) were treated in three different methods (traditional, splitting after liming and shaving after pickling).

2. MATERIAL AND METHOD

2.1. Materials

The following materials have been used in this study;

The 14 pieces of dry salted hides which compose the raw material of the study were provided from Gerede Koza Leather Enterprise. These hides were belonged to the domestic male bovine of the Angus race. No damage was seen on the hides. Hides were divided into two from the neck towards the tail through the belly line and 28 sides of the hides were obtained. The 27 sides of the hides were used in the experiments.

2.2 Method

Samplings from all leathers for all tests were done according to TS EN ISO 2418 standard (8). The test samples were conditioned according to TS EN ISO 2419, at 23 ± 2°C temperature sand 50% ±5 relative humidity (9). The thicknesses of test samples were measured according to TS EN ISO 2589 standard (10) by using Satra-Thickness gauge. In order to evaluate the physical changes of samplings, shrinkage temperature (11), tensile strength and percentage of elongation (12), tear load – single edge tear (13), tear load - double edge tear (14), distension and strength of grain-ball burst test (15) were examined. For the determination of tensile strength, percentage extension, single and double edge tear load, distension and strength of grain Shimadzu AG-IS test instrument was used.

Chemical properties of the leather samples were determined according to: TS EN ISO 4044 Preparation of chemical test samples (16), matter soluble in dichloromethane and free fatty acid content (17), chromic oxide content (18) and degree of tannage (19).

In the study, chrome, vegetable, wet-white tanning types are used and try out pattern is constructed by applying traditional, splitting after liming, shaving after pickling tanning methods. Chrome, vegetable, wet-white tanning recipes of the leathers are given in Tables 1, 2, 3. The methods of tanning, traditional, splitting after liming, shaving after pickling are given in Table 4.

Side leathers were mixed and then, according to trial pattern, in the manner of three renewal, they were processed with nine different treatment formulas (traditional chrome tanning, splitting after liming chrome tanning, shaving after pickling chrome tanning, traditional vegetable tanning, splitting after liming vegetable tanning, shaving after pickling vegetable tanning, traditional wet-white tanning, splitting after liming wet-white tanning and shaving after pickling wet-white tanning).IBM SPSS 16. 0 prompt package program was used for evaluating the obtained results in the survey. Evaluations were followed according to one way variance analyze test.

Table 1. Chrome tanning recipe

TREATMENT STAGE	FLOAT (%)	CHEMICAL	TEMPERATURE (°C)	TIME	CONTROL
Pickling	100	Water	22		
	10	Sodium chloride		5’	Bome: 7
	0.3	Sodium format			
	0.5	Sulphited oil			
	0.8	Formic acid		30’	
	1.3	Sulfuric acid		3*15’+180'	Ph: 2.8-3.2
Tanning	8	Chrome		120'	
Basification	0.5	Sodium format		30'	
	0.45	Magnesium oxide		8h	Ph:3.8-4

Table 2. Vegetable tanning recipe

TREATMENT STAGE	FLOAT (%)	CHEMICAL	TEMPERATURE (°C)	TIME	CONTROL
Pickling	100	Water	22		
	10	Sodium chloride		5’	Bome:7
	0.3	Sodium format			
	0.5	Sulphited oil			
	0.4	Formic acid		30’	
	0.4	Formic acid		30’	
	0.4	Sulfuric acid		3*15+180'	pH: 4
Tanning	2	Phenolicsyntan		20'	
	5	Mimosa		30'	
	5	Quebracho		30'	
	5	Mimosa			
	1	Trotter fat		30’	
	5	Quebracho		30'	
	5	Mimosa		30'	
	5	Quebracho		30'+15 h	
	1	Formic acid		60'	
	+100	Water	22		
	0.5	Formic acid		30’	pH:3.8

Table 3. Wet-white tanning recipe

TREATMENT STAGE	FLOAT (%)	CHEMICAL	TEMPERATURE (°C)	TIME	CONTROL
Pickling	100	Water	22		
	10	Sodium-chloride		5’	Bome: 7
	0.3	Sodium formate			
	0.5	Sulphited oil			
	0.8	Formic acid		30’	
	1.3	Sulfuric acid		3*15’+180'	pH: 2.8-3.2
Tanning	7	Phenolic syntan		120'	
	8	Modified glutaraldehyde		12 h	
	3	Sodium formate		3*15’+150'	pH: 3.8-4

Table 4. Tanning methods

Traditional	Splitting after liming	Shaving after pickling
Soaking	Soaking	Soaking
Unhairing-Liming	Unhairing-Liming	Unhairing-Liming
Fleshing	Fleshing	Fleshing
—	**Splitting**	—
Deliming	Deliming	Deliming
Bating	Bating	Bating
Pickling	Pickling	Pickling
—	—	**Shaving**
Tanning	Tanning	Tanning
Shaving	**Shaving**	**Shaving**
Neutralization	Neutralization	Neutralization
Retanning-Dyeing	Retanning-Dyeing	Retanning-Dyeing
Fat liquoring	Fat liquoring	Fat liquoring
Fixation	Fixation	Fixation
Setting Out	Setting Out	Setting Out
Drying	Drying	Drying
Staking	Staking	Staking
Trimming	Trimming	Trimming
Measuring	Measuring	Measuring

3. RESULTS AND DISCUSSION

Considering these expectations the physical tests and chemical analyzes results are given and discussed below.

3.1. Physical Test Results

Physical test results of the upper leathers are given in Table 5.

Acceptable quality standards recommended by United Nations Industrial Development Organization (UNIDO), for chrome tanned shoe upper side leathers 20 N/mm^2 and for vegetable tanned shoe upper side leathers are 25 N/mm^2 for minimum tensile strength, chrome or vegetable tanned shoe upper leathers are 40% for minimum elongation and chrome tanned shoe upper side leathers are 40 N/mm for minimum tear strength.

According to tanning method; when the shrinkage temperature is investigated, there has been seen statistical difference only at vegetable tanning and it is made firm that the most suitable tanning method is splitting after liming. Tensile strength is seen statistically different at the chrome and wet-white tanning methods and it is considered that the most suitable tanning method is shaving after pickling. When the determination of percentage of elongation is investigated, statistical difference is seen at the types of vegetable and wet- white tanning and it is made firm that the most suitable tanning method at both of the tanning method is splitting after liming. Single edge tear strength is found statistically different at all tanning methods and it is determined that the most suitable tanning methods are splitting after liming and shaving after pickling at chrome tanning method, on the other hand at the vegetable and wet- white tanning methods, it is determined that the most suitable tanning method is only shaving after pickling. Double edge tear strength is found statistically different at chrome and wet-white tanning methods and it is determined that the most suitable tanning method is shaving after pickling at both tanning methods. Cracking strength and cracking elongation are found statistically different at chrome and wet-white tanning types and it is determined that the most suitable tanning method is shaving after pickling at both tanning types. Bursting strength is found statistically different at chrome and wet-white tanning types and it is determined that the most suitable tanning method is shaving after pickling at both tanning types. Bursting elongation is found statistically different at chrome and vegetable tanning types and it is determined that the most suitable methods are splitting after liming and shaving after pickling at chrome tanning method, on the other hand at vegetable tanning type, it is considered that the most suitable method is splitting after liming.

At all physical tests on which statistical differences are seen at the results of the survey, it is determined that splitting and shaving treatments before tanning have better results comparing to the traditional method. It is considered that the reason of this is to reduce the leather thickness thanks to splitting and shaving treatments before tanning and beginning from this stage, the increase of chemical substance penetration at the leather.

Table 5. Physical Test Results

			CHROME TANNED LEATHERS			VEGETABLE TANNED LEATHERS			WET- WHITE TANNED LEATHERS		
Test			T	S.L	S.P	T	S.L	S.P	T	S.L	S.P
Shrinkage Temperature	°C	Min	122.60	120.15	121.00	77.20	89.40	84.25	94.75	98.60	95.10
		Max	125.75	122.95	123.05	78.75	91.60	87.40	103.05	99.55	99.60
		X ± S_E	124.22±0.91^{a}	121.37±0.83^{a}	122.10±0.60^{a}	77.93±0.45^{a}	90.55±0.64^{c}	85.88±0.91^{b}	98.65±2.41^{a}	99.10±0.28^{a}	97.38±1.30^{a}
		S_D	1.58	1.44	1.03	0.78	1.10	1.58	4.17	0.48	2.25
Tensile	Strength (N/mm^2)	Min	15.75	12.96	17.28	10.00	7.30	10.39	7.24	10.24	15.26
		Max	16.14	15.85	18.64	11.34	10.11	12.08	8.12	12.74	16.50
		X ± S_E	15.90±0.12^{a,b}	14.80±0.92^{a}	17.76±0.44^{b}	10.46±0.44^{a}	9.14±0.92^{a}	10.97±0.56^{a}	7.75±0.26^{a}	11.89±0.82^{b}	15.72±0.39^{c}
		S_D	0.21	1.60	0.76	0.77	1.60	0.96	0.46	1.43	0.68
	Elongation (%)	Min	55.00	59.11	56.77	41.63	49.74	43.97	53.94	57.18	56.11
		Max	60.36	63.34	58.42	43.16	52.35	45.80	55.21	62.07	56.59
		X ± S_E	57.41±1.57^{a}	61.57±1.27^{a}	57.44±0.50^{a}	42.19±0.49^{a}	50.65±0.85^{b}	44.98±0.54^{a}	54.46±0.38^{a}	59.12±1.5^{b}	56.32±0.14^{a,b}
		S_D	2.72	2.20	0.87	0.85	1.47	0.93	0.67	2.60	0.24
Single Edge Tear	Strength (N/mm)	Min	48.03	51.61	51.70	21.19	16.25	27.42	25.18	41.99	46.70
		Max	49.57	54.96	53.23	21.37	17.03	29.82	29.90	42.25	47.97
		X ± S_E	48.67±0.46^{a}	52.77±1.10^{b}	52.27±0.48^{b}	21.26±0.055^{b}	16.55±0.24^{a}	28.41±0.72^{c}	28.11±1.48^{a}	42.15±0.08^{b}	47.18±0.40^{c}
		S_D	0.80	1.90	0.84	0.09	0.42	1.25	2.56	0.14	0.69
Double Edge Tear	Strength (N/mm)	Min	114.23	109.87	123.90	49.90	47.24	61.28	66.59	74.70	107.83
		Max	115.65	116.02	126.60	50.96	63.30	69.74	81.90	95.45	116.70
		X ± S_E	115.01±0.42^{a}	113.77±1.96^{a}	125.59±0.85^{b}	50.27±0.35^{a}	57.89±5.32^{a}	64.15±2.80^{a}	71.77±5.07^{a}	88.25±6.78^{a}	110.97±2.87^{b}
		S_D	0.72	3.39	1.47	0.60	9.22	4.84	8.78	11.74	4.97
Cracking	Strength (kgf)	Min	27.00	21.50	34.50	7.00	6.00	9.00	11.50	9.00	28.00
		Max	42.00	24.00	56.50	19.00	17.50	12.00	13.00	21.50	44.00
		X ± S_E	33.00±4.58^{a,b}	22.83±0.73^{a}	45.33±6.35^{b}	13.17±3.47^{a}	12.17±3.35^{a}	10.83±0.93^{a}	12.17±0.44^{a}	15.50±3.62^{a}	36.83±4.70^{b}
		S_D	7.94	1.26	11.00	6.01	5.80	1.61	0.76	6.26	8.13
	Distension (mm)	Min	8.89	8.66	9.76	6.03	7.60	6.82	8.50	7.15	8.91
		Max	9.55	8.83	10.84	7.65	8.06	6.89	8.79	8.40	9.80
		X ± S_E	9.31±0.21^{a}	8.73±0.50^{a}	10.46±0.35^{b}	7.03±0.51^{a}	7.80±0.14^{a}	6.86±0.02^{a}	8.62±0.088^{a,b}	7.82±0.36^{a}	9.40±0.26^{b}
		S_D	0.36	0.087	0.604	0.88	0.24	0.04	0.15	0.63	0.45
Bursting	Strength (kgf)	Min	44.00	48.00	53.50	19.00	9.00	15.50	17.00	22.50	42.00
		Max	51.00	49.50	57.00	25.50	30.00	21.50	23.50	39.00	53.50
		X ± S_E	47.17±2.05^{a}	48.67±0.44^{a}	55.00±1.04^{b}	21.83±1.92^{a}	20.83±6.21^{a}	19.33±1.92^{a}	20.17±1.88^{a}	29.83±4.85^{a}	48.67±3.44^{b}
		S_D	3.55	0.76	1.80	3.33	10.75	3.33	3.25	8.40	5.97
	Distension (mm)	Min	10.41	11.27	11.17	8.22	9.34	8.37	10.36	9.95	10.14
		Max	10.99	11.72	11.71	8.75	9.60	8.62	11.13	10.61	10.56
		X ± S_E	10.62±0.18^{a}	11.52±0.13^{b}	11.42±0.16^{b}	8.56±0.17^{a}	9.48±0.08^{b}	8.46±0.08^{a}	10.69±0.23^{a}	10.35±0.20^{a}	10.37±0.12^{a}
		S_D	0.32	0.23	0.27	0.29	0.13	0.14	0.40	0.35	0.21

,b,c; the differences between the averages indicated by different letters in the same column are important ($p<0.05$)
*T: Traditional S.L: Splitting after liming S.P: Shaving after pickling

3.2. Chemical Test Results

Physical test results of the upper leathers are given in Table 6.

Table 6. Chemical Test Results

			CHROME TANNED LEATHERS			VEGETABLE TANNED LEATHERS			WET- WHITE TANNED LEATHERS		
Test			T	S.L	S.P	T	S.L	S.P	T	S.L	S.P
Matter Soluble in Dichloromethane and Free Fatty Acid Content	%	Min	8.03	4.08	4.95	6.72	7.52	6.82	6.92	5.53	7.02
		Max	8.07	6.07	5.08	7.11	10.27	7.20	7.10	7.49	7.25
		X ± S_E	8.05±0.01[b]	5.07±0.57[a]	5.00±0.04[a]	6.93±0.11[a]	8.87±0.79[a]	7.03±0.11[a]	7.00±0.05[a]	6.56±0.57[a]	7.16±0.07[a]
		S_D	0.02	0.1	0.07	0.2	1.38	0.19	0.09	0.98	0.12
Chromium Oxide Content	%	Min	3.36	3.53	3.40						
		Max	3.70	3.60	3.68						
		X ± S_E	3.53±0.10[a]	3.57±0.02[a]	3.54±0.08[a]						
		S_D	0.17	0.04	0.14						
Degree of Tannage	%	Min				49.81	50.42	34.92			
		Max				54.06	57.04	36.29			
		X ± S_E				51.83±1.23[b]	53.76±1.91[b]	35.78±0.43[a]			
		S_D				2.13	3.31	0.75			

a,b,c; the differences between the averages indicated by different letters in the same column are important ($p<0.05$)
*T: Traditional S.L: Splitting after liming S.P: Shaving after pickling

Acceptable quality standards recommended by United Nations Industrial Development Organization (UNIDO), for chrome tanned shoe upper side leathers are 9% maximum of the amount of fat in the leather and for vegetable-tanned upper leathers should be between 15-25%, for shoe upper side leathers are 2.5% minimum of the amount of chromic oxide.

When the average values, belonging to the matter soluble in dichloromethane and free fatty acid content, at chemical analyzes are examined; it is seen that the results at chrome tanned leathers are suitable for the UNIDO values and the results at vegetable tanned leathers are lower than the UNIDO values. It is thought that the reason of this is because the treatment is not changed except for the tanning stage at our study and therefore anointment substances peculiar to vegetable tanning are not used. On the other hand, in terms of wet-white tanning type, it is seen that there is not a significant difference between the tanning methods, statistically.

All the obtained values of the amount of chromium oxide are found suitable for the UNIDO values when the tanning methods in chrome tanned leathers are examined. It is thought that as Toptaş states while dealing with the properties of chrome salts, because of the usage of chrome salts with small molecules at tanning, there is not a statistically significant difference between the tanning methods (20).

At the booklet named Pocket book for the leather technologist, it is said that the number of tanning at vegetable tanned leathers must be greater than 50 (21).

When the tanning methods at vegetable tanned leathers are examined, the obtained values of the numbers of tanning are found convenient according to the splitting after liming and inconvenient according to the shaving after pickling method. The reason of this is thought that, at the treatment of shaving after pickling, automatic shaving machines are not used because they ruin the collagen structure of the leathers by warming them due to their high cycles, that is why, the shaving treatment is obliged to be done with the traditional shaving machines, so tanning number outcomes lower because sensitive shaving cannot be done and this gives birth to over shaving of reticular layer.

4. CONCLUSION

It is seen that splitting after liming or shaving after pickling increases the physical strength of leathers at chrome, vegetable, wet-white tanning when compared to the traditional tanning method.

Matter soluble in dichloromethane and free fatty acid content are equal to the standards at the chrome tanned leathers, lower from the standards at the vegetable tanned leathers. At wet-white tanned leathers, there is not statistically significant difference between the tanning methods and in this subject, there is no definite standard relating to wet-white leathers. The percentage of chromium oxide is found higher than standard values at all the tanning methods. Tanning number is detected high at the method of splitting after liming and is detected low at the method of shaving after pickling comparing to traditional method.

It is really important for a company, to increase the quality of the product that they produce or to reduce the cost as the rivalry ascends day after day. In this study, both the increase of quality, by applying splitting or shaving to leathers before tanning, and the decrease of cost, especially on the ground that the tanning materials are used quite little, are the subject. Thanks to decreasing the thicknesses of leathers before tanning, giving lesser untanned wastes to the environment and evaluating flesh splits of liming are also important.

When considering the environment laws which are carried out firmly in recent years and both difficulty and high cost of making tanned wastes harmless to livings and environment, it can be seen that the decrease of these types of wastes is really important for leather sector and our world.

* This study has been produced from the PhD thesis of Levent İnanç.

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