(REFEREED RESEARCH)

POSSIBILITIES OF USAGE OF ALKALI ALUMINOSILICATES AS TANNING MATERIAL IN CHROMIUM-FREE LEATHER PRODUCTION

KROMSUZ DERİ ÜRETİMİNDE TABAKLAMA MADDESİ OLARAK ALKALİALÜMİNYUM SİLİKATLARIN KULLANIM OLANAKLARI

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Received: 04.01.2015 Accepted: 01.03.2016

ABSTRACT

The leather industry, in foundation of Turkish economy, is a labor-intensive branch of industry that takes an important part among textile and related branches of industry; by processing hides or skin of bovines and ovines, makes them eligible for production of various manufactured goods. The present leather products involves many varieties like saddlery, sole leather, technical work ware, hides and furs, leather clothing etc. However, alongside these variations, demands for leather products across the globe are influenced from strategies of societies aiming environmental protection. Developing environmental consciousness, increase of sensibility for ecologic issues and legal legislations leads industrialists to choose methods that have less damage to environment and to produce goods obtained by these methods. Increased environmentalism propagandas have influence on derivation of new leather types named as "Eco-leather", "Bio-leather", "Chromium free-leather". In leather production, this worldwide searching issue proposes new studies for the agenda. New products and production processes designs in which bestavailable techniques, clean technologies are used and environmental impacts are minimised during along an innovative conversion. In this study, various tanning combinations were implemented among alkali aluminosilicates which is a kind of zeolite, vegetable and vegetable-synthetic tanning matters and aluminum triformate. It was attempted to specify whether alkali aliminum silicates have tanning effect or not, and which combination provides the most appropriate results as for tanning quality. Leather samples that were procured in pursuant of these combined tanning methods were tested and analyzed in physical and chemical terms, the results were evaluated by comparing according to accepted standards for garment leathers.

Keywords: Chromium-free leather, zeolite, alkali aluminosilicate, ecological tanning

ÖZET

Deri sanayi, Türkiye ekonomisinin temel yapısı içerisinde, tekstil ve benzer sanayi dalları arasında önemli bir yer alan, küçük ve büyükbaş hayvanların derilerini işleyerek çeşitli mamul eşya yapımına elverişli hale getiren emek yoğun bir sanayi dalıdır. Bugün üretimi yapılan deri mamulleri, saraciye eşyası, kösele, teknik iş eşyası, postlar ve kürkler, deri giyim eşyası vb. olmak üzere pek çok çeşidi kapsamaktadır. Ancak bu varyasyonların yanı sıra dünya genelinde deri mamullerine yönelik talepler, toplumların çevre korumaya yönelik stratejilerinden de etkilenmektedir. Gelişen çevre bilinci, ekolojik sorunlara yönelik hassasiyetin ve yasal mevzuatların artması, sanayicileri çevreye daha az zarar veren yöntemlerin seçimine ve bu yöntemlerle elde edilen mamullerin üretimine teşvik etmektedir.Artan çevrecilik propagandaları "Eko-deri","Bio-deri","Kromsuz-deri" olarak adlandırılan yeni deri tiplerinin ortaya çıkmasında etken olmaktadır. Deri üretiminde, dünya genelinde söz konusu olan bu arayış yeni araştırmaları gündeme getirmektedir. Mevcut en iyi tekniklerin, temiz teknolojilerin kullanıldığı ve çevresel etkilerin minimize edildiği yeni ürün ve üretim prosesleri tasarımı inovatif bir dönüşümü de beraberinde getirmektedir. Bu araştırmada, bir tür zeolit olan alkali alüminyum silikatları ile bitkisel, bitkisel-sentetik tabaklama maddeleri ve alüminyumtriformiat arasında çeşitli tabaklama kombinasyonları uygulanmıştır. Alkali alüminyum silikatların tek başına tabaklayıcı etkisi olup olmadığı ve tabaklama niteliği açısından hangi kombinasyonun en uygun sonuçları sağladığı belirlenmeye çalışılmıştır. Bu kombine tabaklama yöntemlerine göre elde edilen deri örnekleri fiziksel ve kimyasal açıdan test ve analiz edilmiş, sonuçlar giysilik deriler için kabul edilen standartlara göre karşılaştırılarak değerlendirilmiştir.

Anahtar Kelimeler: Kromsuz deri, zeolit, alkali alüminyum silikat, ekolojik tabaklama.

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1.INTRODUCTION

Tanning, one of the most important stage in leather producing, is determined as to convert raw hide to processed leather in technical processes (1).Chemicals used in this processes and these are termed as “tanning materials”. These chemicals can be mineral matters like chromium and aluminium, and particularly vegetable and synthetic tannins.

Chromium, within mineral tannins, is one of the tanning materials that has the features expected from leather products and chromium tannin is used as a standart tanning method worldwide in leather production. However, it's environmental impact assesments are in high levels based on toxic features. For this reason, legislative regulations related to chromium are gaining importance in REACH ((Registration, Evaluation, Authorization and restriction of Chemicals) and CLP (Classification Labelling Packaging) (2,3).

Researches oriented less or zero chromium usage have increased and new eco-friendly production systems have became a current issue. In addition to this, complex and strict legislation in the fields of ecotoxicology, necessitated optimizing chemicals used in leather production.

Researches carried out with the use of an oligomeric melamine-formaldehyde resin and resorcinol pre-polymer as pretanning materials for the production of chromium free leathers, and new titanium based tanning material, obtained from processing wastes from the industry of nonferrous metals are actual examples (4).

At the present time, possibilities of chromium-free production are studied for clothing and shoe leather besides the other processed leathers. Chromium-free methods have gained commercial importance especially in furnishing leathers produced for automotive .

Another researches, intitled as green and eco-friendly methods, are tanning processes carried out with D-Lysine glutaraldehyde complex. This tanning process has the cost advantage sdue tothe possible decrease in chemicals consumptions and net saving from the reducede fluent treatment costs (5).

Studies, intended chromium-free leather production, deliberate on new techniques make pre-tanning with aluminium salts. These are named as “wet-white” method. Being an alternative to chromium makes it more remarkable.

Wet-white tanning process, carried out with a kind of zeolite aluminium silicates, have proved that this mineral is able to used as a tanning material by combining with the others.

Leathers, tanned with optimisation of production process along sodium aluminium silicates, have advantages like mechanical endurance, stable form etc. by comparison with the other wet-white tanned leathers. It is provided to decreaserepletion, firmness and double bound in sheepskin tanning (6).

Within this research, an array of tanning methods consisted alkaline aliminium silicates and various tanning materials combination are analysed, chemicalanalysis and physical testing applied in leathers obtained from studies, and it is aimed to optimize eco-friendly leather production process enables benefit from new mineral resources and targets solving environmental issues.

2.MATERIAL AND METHOD

2.1.MATERIAL

Pickled Iran sheep skin was used as a research material. 4 cropons areas of sheep skin used for each test and 4 experiments practiced with several combinations.

As the tanning material, particularly alkali aliminium silicate and vegetable and synthetic tanin were used. Alkali alimino silicate is a synthetic zeolite produced with special methods and it’s chemical formula stated as $(Na_2O.Al_2O_{3}.{}_2SiO_2)_{12}.27H_2O$. Produced from natural zeloite, it has stable combination and Al-Si ratio is in expected level in displaying tanning effect. This material is in pure state specifically, can dissolve in organic and inorganic acids. Additionally, it can be reproduced and taning effect can be lifted by modifying (7).

Besides that, for the combined tanning method tests, sulfated quebracho’s commercial powder extract involving 80-82% of tannin, 8-10% of non-tanning matter was used as vegetable tanning material; and as synthetic tannin, phenol based commercial condensation product having a high light fastness, at pH value of 3.5-4.0, involving 45% of dry matter was chosen.

The chemical bonds that tanning agents form with fibers, in other words protein structure, in the leather structure are a series of reactions which determine mechanism of tannery process. It is known that the tanning effect of silicates used in this research occurs within two stages. At the first stage, alkali aluminosilicate tanning matter that is not usable yet in sodalite form, convert to small-granular compounds which are well-soluble with the help of acidic pickled solution. At the second stage, tannery reaction happens chain-formed aluminosilicates which are soluble and in the form of chains, with collagen chains at pH 4.1 (8).

2.2. METHOD

In the research, firstly the stage of process (tannery) of pickled sheep skins chosen as material were realized, then chemical and physical tests were applied to leather samples, properly to TSE standards.

As tanning method during processing of leathers;

- Pre-tanning with sodium aluminosilicate and alkali aluminosilicate tanning (Recipe 1)
- Vegetable/synthetic pre-tanning and alkali aluminosilicate tanning (Recipe 2)
- Pre-tanning with vegetable tanning matters and alkali aluminosilicate tanning (Recipe 3)
- Pre-tanning with aluminum triformate and alkali aluminosilicate tanning (Recipe 4) four different combinations were applied.

In all tests, only tanning process was based and in order not to face differences resulting from pre- and post-tanning processes, only one recipe was used for pre- and post-tanning processes of tests.

Sampling processes were conducted of the leathers obtained according to the recipes presented below to determine physical and chemical features of them, in compliance with the rules determined in TSE standards; and were compared with standard values applying related analysis and tests (9,10,11).The list of applied analysis and tests in the research was given in Table 1.

Table 1. Chemical Analysis and Physical Testing applied to samples

Physical Testing	**Standard**
Determination of tensile strength and percentage extension	TS EN ISO 3376
Determination of tear load	TS 4118-2 EN ISO 3377-2
Measurement of stitch tear resistance	TS EN ISO 23910
Determination of Distersion and Strength of Grain- Ball Burst Test	TS 4131
Shrinkage Temperature	TS 4120 EN ISO 3380
Chemical Analysis	
Determination of pH	TS EN ISO 4045
Determination of fat content	TS 4124
Determination of water content	TS 4127
Determination of Nitrogene and "Hide Substance" of leather	TS 4134
Determination of content of aluminium in leather	TS 4130
Determination of content of silicium in leather	TS 4139

Recipes 1. Pre-tanning with sodium aluminosilicate and alkali aluminosilicate tanning

Process	**%Float**	**Product**	**Temperature °C**	**Time (minute)**	**pH**
De-pickling	25	Water (NaCl, 7° Bé)	30°C	15’	4.5
	1	Alkaline aluminium silicate		60’	
	2	Sodium bicarbonate		150’	
	100	Water	35°C	15’	
Bating	1	Bating enzym		30’	
Washing	200	Water		15’	
Degreasing	25	Water(NaCl,7° Bé)			
	5	Foril			
Wash/x3	100	Water			
Tanning	80	Water(NaCl,7° Bé)			
	2	Sulfited fish oil			
	2	Anionic fatty mater		10’	5.8
	0.7	Formic acid			
	1	Dicarbonic acid			
	1	Alkaline aluminium silicate		10’	3.6
	2	Anionic resin		20’	
	0.9	Sulfuric acid		60’	
	2	Alkaline aluminium silicate			3.9
		(waiting in float during over night ,unloding drum ,pilling)			
		Boiling test			
	250	Water	40°C		
Neutralising	1.5	Sodium bicarbonate			
	8	Combined fatty mater		45’	
	6	Sulfited sulfonated fatty matter			
	10	Product of condensation		15’	
	1	Formic acid			
	200	Water	35°C	15’	
	2	Fatty matter			
		(unloding float,pilling)		30’	

Recipes 2. Vegetable/synthetic pre-tanning and alkali aluminosilicate tanning

Process	**% Float**	**Product**	**Temperature °C**	**Time (minute)**	**pH**
Tanning	80	Water (NaCl,5° Bé)	25°C		
	1	Anionicfatty matter		30’	
		Synthetic Tanin		30’	
	5	Quebracho		120’	4.5
	6	Synthetic Tanin		30’	
	3	Fatty matter		65’	
	6	Alkaline aluminium			
	2	silicate		60’	3.9
		Formic acid		20’	
Washing /x3	0.2				

Recipes 3. Pre-tanning with vegetable tanning matters and alkali aluminosilicate tanning

Process	% Float	Product	Temperature °C	Time (minute)	pH
Tanning	80	Water (NaCl,5° Bé)	25°C		
	1	Anionic fatty matter		30'	
		Quebracho		120'	
	10	Fatty matter			
	6	Alkaline aluminium		60'	
	2	silicate		60'	
				20'	3.9
	0.2	Formic acid			
Washing/x3					

Recipes 4. Pre-tanning with aluminum triformate and alkali aluminosilicate tanning

Process	% Float	Product	Temperature °C	Time (minute)	pH
Tanning	80	Water (NaCl,5° Bé)	25°C		
	2	Sulfited fish oil			
	2	Anionic bate product			
	1	Dicarbonic acid		30'	3.6
	1	Aluminium triformate		20'	
	2	Anionic resin		60'	
	0.9	Sulfiric acide		15'	
	2	Alkali alüminium silicate		120'	3.9
Washing/x3					

3. FINDINGS AND DISCUSSION

3.1. Physical Tests

One of the most important features of processed leathers which are obtained from raw hides by being subjected to a series of mechanical processes and different chemical matters is strength. Three dimensional structure of a leather fiber shows the feature of a network that provides elongation under a force and recovering to the first case after the force. However, it is known that any change occurring in leather fiber affects strength. Therefore, the most reliable information about usability of processed leather can be revealed through researching its strength.

The physical tests listed in Table 1 are the check methods used for determining strength features of garment processed leather. Therefore, toward sheep skins preferred as research material and applied tannery combinations, strength evaluation criteria of garment leathers were based on; and the obtained results are presented in Tables 2 and 3.

The tensile strength and elongation values obtained in the research are varying between 125.5 daN/cm² and 263.5 daN/cm². The smallest tensile strength value for chrom tanned garment leather is stated as 100 daN/cm² by UNIDO (12).

According to this, strength values of all the leather samples are within the required level and the leathers obtained through vegetable-synthetic tanning method have the highest value with 199.3daN/cm^2 average. This value shows that tanning agents are highly bonding with leather, but in this tanning combination that have high fat ratio, it can be considered that high fat ratio provides fibers glide onto each other and this influence tensile strength positively.

Table 2. The Results of Physical Testingof Leather Samples

Combination of Tanning	Tensile strenght daN/cm²			Elongation %			Tear strenght daN/cm			Stitch tear resistance daN/cm		
	min	max	avg	min	max	avg	min	max	avg	min	max	avg
Tanning with alkali aluminium silicate	155.5	205.0	179.8	68.0	72.0	69.7	30	55.0	39.3	79.94	98.61	87.58
Vegetal tanning+ tanning with alkali aluminium silicate	125.5	158.5	139.0	67.0	79.0	74.0	30	37.5	31.8	86.93	96.88	90.66
Aluminiumtriformate+ Tanning with alkali aluminium silicate	170.4	218.4	194.4	75.0	78.0	72.5	35	42.5	38	107.09	129.36	112.60
Vegetal-synthetic tanning+ Tanning with alkali aluminium silicate	163.5	263.5	199.3	52.0	61.0	55.2	32.5	50.0	38.1	110.26	124.57	116.35

Elongation at break values of all the samples are varying between 52% and 79% and the mean value is 67.8%. According to UNIDO, suggested maximum elongation for garment leathers that are chromium tanned is 60%. In the tannery tries done, with 74%, vegetable tanning matters and alkali aluminosilicate combination has the highest value.

Like garment and upper leather, check for resistances to stitch tear of leather products which loads fall on their stitches during usage, has to be done.That check is done with stitch tearing strength tests to the leather (13).

According to the values stated by UNIDO for chromium tanned garment leathers, the suggested minimum stitch tearing strength is 25 kgf/cm.

Stitch tearing strength for furniture leathers are stated as between 69 daN/cm and 83 daN/cm in sodium aluminosilicate and aldehyde tannery studies. It is known that these values are varying between 75-200 daN/cm for upper leathers (14).

In the research, obtained stitch tearing strength values are within the expected values, and as in tensile strength, the highest value belongs to semi-vegetable tanning matters and alkali aluminosilicate combination with the value of 116.3 daN/cm. According to the results, it seen that the tanning ability of this combination is higher than the others.

As one of the quality control test methods based on strength, tearing strength was also tested for leather samples in the research and it was found that these values are varying between 30 daN/cm and 55 daN/cm with mean value of 36.8 daN/cm.

Tearing strength value suggested by UNIDO for chromium tanned garment leathers is 15 kgf/cm minimum, and for aluminum tanned gloving leathers is 25 kgf/cm minimum. It is seen that the obtained results are within the limits of these values and are at the expected level for garment leather.

Grain elongation ability is a quality control criterion which is determined with the help of skin or roller coat blast over height of toe-box. This method is used for especially shoe upper leather, but is suggested also for other light leathers.

The obtained grain cracking resistance and corresponding elongation values in the research are given in Table 3. These values are varying between 16.80 daN/cm² and 31 daN/cm², and elongation values are between 13.14 mm and 16.84 mm.

The highest dermis papillar resistance and tensibility values belong to aluminum triformate and alkali aluminosilicate combination with the values, 27.37 daN and 15.86 mm.

As for grain blast resistances, values are varying between 18.50 daN and 34 daN; and elongation values are between 13.38 mm and 17.79 mm.

It was detected that the highest values among applied tannery combinations, again belong to aluminum triformate and alkali aluminosilicate tanning method with the values 31.12 daN and 16.72 mm.

Table 3. The results of physical testing of leather samples

Combination of Tanning	Grain cracking resistance daN/cm²			Elangotion mm			Grain blast resistance daN			Elangotion mm		
	min	max	avg	min	max	avg	min	max	avg	min	max	avg
Tanning with alkali aluminium silicate	19.50	31	26.25	13.96	15.90	14.63	24.50	30.5	29.63	14.54	16.47	15.40
Vegetal tanning+ tanning with alkali aluminium silicate	17.50	28	21.87	13.38	14.97	14.28	18.50	28	23.25	13.38	15.62	14.66
Aluminiumtriformate+ Tanning with alkali aluminium silicate	26	28.5	27.37	14.96	16.84	15.86	27	34	31.12	15.44	17.79	16.72
Vegetal-sentetic tanning+ Tanning with alkali aluminium silicate	16.80	26.35	15.86	13.14	14.55	13.94	24.5	29	26.37	13.86	14.92	14.49

Table 4. The shrinkage temperaturs of leather samples

Combination of Tanning	Shrinkage Temperaturs °C		
	min	max	avg
Tanning with alkali aluminium silicate	75	76	75
Vegetal tanning+ tanning with alkali aluminium silicate	77	79	78
Aluminiumtriformate+ Tanning with alkali aluminium silicate	82	88	85
Vegetal-synthetic tanning+ Tanning with alkali aluminium silicate	79	84	82

The behaviors which tannery processed leathers show against temperature provide acquisition of information about variance and bonding abilities of tanning agents in leather section and interfibrillar area. One of the physical test methods that are used for this purpose is shrinkage temperature determination.

Shrinkage temperature of raw material which has not been subjected to any process varies between 60-65 °C, and for pelt it is changing between 40 and 60 °C. It is known that there is directly proportional relation between density of cross link reactions occuring in fine structure of leather and tannage effect. This value is 70-80 °C in vegetable tanned leathers, 75-85 °C in chromium tanned leathers and 60-70 °C in semi-tanned leathers (15).

In tannery studies done with sodium aluminosilicate, it was reported that basic aluminum compounds and poly-silica-acids show tanning effect and shrinkage temperature is about 70 °C (16).

The shrinkage temperature values obtained in the research are within expected limits and the leathers which were tanned with aluminum triformate and alkali aluminosilicate combination have the highest shrinkage temperature value with mean of 85 °C. This shows that variance and bonding abilities of tanning agents used in leather section are better than other combinations.

3.2. Chemical Analysis

To determine quality features of leather product, chemical analyses are important as much as physical analyses. According to production stage features and intended use of leather, the chemical analyses are determined. In this research a series of chemical analyses were applied to the leather samples obtained from research materials for determining values of pH, fat, moisture, leather matter, aluminum and silicium. The obtained results are shown in Table 5 and 6.

Table 5. The results of chemical analysis of leather samples

Combination of Tanning	Hide substance of leather %			Aluminium %			Silicium ppm		
	min	max	avg	min	max	avg	min	max	avg
Tanning with alkali aluminium silicate	45.65	48.50	46.93	0.18	0.38	0.29	23.05	24.0	23.25
Vegetal tanning+ tanning with alkali aluminium silicate	41.71	46.54	44.82	1.38	2.05	1.69	37.75	47.2	40.58
Aluminiumtriformat e+ tanning with alkali aluminium silicate	61.24	69.06	64.87	1.09	1.83	1.30	16.70	16.72	16.71
Vegetal-synthetic tanning+ tanning with alkali aluminium silicate	43.57	51.81	46.61	0.57	0.96	0.75	15.27	15.95	15.61

pH values of leather products should be within some limits in order not to cause any negative effect during use. UNIDO stated that this value for garment leathers should be under pH value of 3.5 for “1/20” extract in water; and if pH value is over 4, the difference number should not exceed 0.7.

Combination of Tanning	pH			Fat %			Water content %		
	min	max	avg	min	max	avg	min	max	avg
Tanning with alkali aluminium silicate	4.24	4.44	4.24	16.73	22.18	27.0	4.44	5.07	4.77
Vegetal tanning+ tanning with alkali aluminium silicate	6.16	6.24	6.20	11.91	35.30	12.25	5.01	6.89	6.10
Aluminiumtriformate+ tanning with alkali aluminium silicate	4.71	4.96	4.82	17.06	17.67	18.75	4.96	6.33	5.66
Vegetal-synthetic tanning+ tanning with alkali aluminium silicate	4.26	4.97	4.61	46.56	62.17	54.36	4.52	5.20	4.70

As seen in Table 5, pH values of leather samples obtained in the research are varying between 4.24 and 6.20.

Natural fat rate in different types of raw materials differ (2-10% in bovine, 3-15% in goat, up to 40% in sheep). This natural fat accumulates in specific areas of skin and is solid in the room temperature. It is necessary to lift up most part of this fat and to distribute homogeneously in leather section during leather production. Otherwise, oil leakage and malodor may occur in the product leather (17).

For this reason, fat determination on product leathers is one of important chemical analyses. In the research, percentage (%) fat values obtained from leather samples are varying between 11.91 and 62.17 % and the mean value is 28.09 %.

As seen in Table 6, fat ratios in the leathers which were obtained through vegetable-synthetic, vegetable tanning materials and alkali aluminosilicate combinations are at very high values; and it is foreseen that oil leakage or oil stain may occur in these product leathers.

Determination of moisture values which take place in chemical analyses scope is applied to all product leathers, because especially it is an effective factor on physical strength of leathers. Moisture quantity is not a quality factor alone, though, it is a criterion determined in researches.

It was stated that in the researches done about the leathers processed through valex-aluminum tanning method, the obtained moisture values for garment leathers were varying between 16.5% and 14.10%. For the leathers processed through mimosa-aluminum tanning method, it was about 15% (18).

The moisture values obtained from the researched tanning matter combinations are varying between 4.44% and 6.89%, and average is 5.3%; it is seen that these values are under expectation for an garment leather product.

Leather matter determination is the determination of fibrillary proteins, namely collagen, calculated over total nitrogen. During production processes, leather matter ratio decreases through minerals, organic tannins, fats etc. which are issued to leather. Therefore, decision about leather quality through being based on only leather matter is difficult. Because, existence of cross links among collagen molecules is more important than that leather protein shows a high value.

Leather matter amounts obtained from leather samples are varying between 41.71% and 69.06%; and the highest value is at aluminum triformate and alkali aluminosilicate tanning combination with 64.87%. This is a proof of existence of cross links between used tanning matter combination and collagen.

On the other hand, tanner mineral oxide amount makes it possible to come to some conclusions about tannery. It generates cross links between mineral matter given to the bath for tannery and collagen’s reactive groups and turns raw hide into non-spoiling case (19).

In tries of applied tannery combinations, vegetable tanning matters and alkali aluminosilicate tanning with ratio of 1.69 was found to have the highest aluminum oxide value.

In silicium determination, chromatographic methods were utilized and the analysis was done in ICP (Emission Spectrometer Portable) device; it was determined that obtained silicium values were varying between 15.61 ppm and 23.25 ppm, and average value was 17.78 ppm.

The highest silicium value belongs to the leathers tanned with vegetable tanning matters and alkali aluminosilicate and it is 40.58 ppm. This result shows that alkali aluminosilicates which form alumosilicates in acidic pH area are compatible with vegetable tanning matters and this combination may form a better bond with leather structure.

4. RESULT

In this research, it was aimed to determine the tanning possibilities of the combinations between alkali alumino silicate a kind of zeolite, vegetal tanning, vegetal-synthetic tanning and aluminum triformate and the utility of these combinations in garment leather production.

When the results were evaluated comparatively, it was determined that the combined tannery method which has the most appropriate analysis results and tanning ability with regard to garment leather production is aluminum triformate and alkali aluminosilicate tanning method.

The tries done as part of the research can be varied by means of changing tanning matter ratios within the same combinations, and utilization opportunities from alkali aluminosilicates as an alternative method for chromium-free environment friendly processed leather production can be increased.

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