Reduction of Cr (VI) Formation in Leather with Herbal Extracts

by

Roza Mirzamuratova,[1] Eser Eke Bayramoğlu[2]* and Gulzinat Yeldiyar[1]
[1]*M. Auezov South Kazakhstan University, Textile and Food Engineering High School,*
Technology and Design of Light Industry Products Department
Shymkent, Kazakhstan
[2]*Ege University, Faculty of Engineering, Department of Leather Engineering*
35100 Bornova - Izmir ,Türkiye

Abstract

This study investigates the effects of extracts from natural products such as oak bark, and onion peel, on the formation of Hexavalent Chromium (chromium (VI)) or (Cr (VI)) in leather during the finishing process. To enable chromium (VI) formation, finished leather samples were aged under various conditions, including exposure to UV light. The amount of chromium (VI) in each leather sample was measured using a PC UV-Visible spectrophotometer at 540 nm based on the ISO/FDIS 17075 standard method. The results showed that extracts from *Quercus cortex,* and *Allium cepa* significantly reduced chromium (VI) formation in the leather under all aging conditions.

Introduction

Chrome tanning is still the most important and widely used method of tanning in the leather industry. The presence of Cr (VI) in leather has attracted great attention in the modern world as environmental protection requirements and safety regulations became increasingly strict. There are risks when converting Cr(III) to Cr (VI) form in the production, storage, transportation and use of chrome-tanned leather, however more than 90% of the leather in the world is processed using chromium salts because of the facile technology, process reliability and high technological and operational properties of the finished leather.[1,2] However, since 1994 when traces of hexavalent chromium were first detected in leather products, chromium-tanned leather attracted increasing attention[3]as hexavalent chromium can cause cancer, skin allergies, liver and kidney necrosis.[4] The European Union(EU) countries even have zero tolerance policies.[5] Nevertheless, chromium salt in its trivalent form (basic chromium sulfate, $Cr(OH)SO_4$ is used in tanning. Chromium-tanned leather imparts excellent hydrothermal stability due to the stable Cr^{3+} complexes. The stable cross-linked structure is formed through covalent bonds between Cr^{3+} and the side-chain ionized carboxyl groups of collagen proteins.[6] Cr (VI) is not used in any step of leather manufacture; therefore, the emergence of hexavalent chromium in leather products should be explained. Numerous studies focused on processing, auxiliaries,[7] temperature,[8] photoaging,[9] humidity,[10] and other factors in the leather manufacturing process were performed to understand the formation of hexavalent chromium. It was found that peroxide and free radicals (ROO·, RO· and·OH) generated by unsaturated fatliquoring agents, photoaging and temperature, play important roles in promoting the chromium (III) oxidation reaction.[11] Therefore, many antioxidants and reducing agents are used in leather processing with the goal of blocking the free-radical chain oxidation and reducing the produced Cr (VI). Taking into account that antioxidative chemicals in leather production can be a solution to prevent the formation of Cr (VI), it is important to investigate the content of these products and their effect on the leather. Every extra chemical used in leather processing has a different effect on the environment and brings extra costs to production. Within the framework of sustainable production, the use of herbal products at various stages of leather treatment is becoming increasingly important.[12-20] Vegetable tannins (condensed and hydrolysable) have a strong inhibitory effect on the Cr^{3+} oxidation in leather. The greater number of hydroxyl groups on the single-ring polyhydroxy phenol results in a stronger inhibitory effect of α-H oxidation. When the same number of hydroxyl groups are on the single-ring polyhydroxy phenols, o-hydroxy phenols has a stronger inhibition than that of p-hydroxy phenols.[21]

Although there are many studies investigating the effect of herbal extracts on Cr (VI) formation in the wet-end treatment, the extracts used in this research were applied to the leather during the finishing stage. It is important to use natural products as an alternative to chemical products to ensure sustainability in the leather industry.

EXPERIMENTS

Materials and Methods

For the study, bovine leather processed by the Turan-Skin factory, located in Kazakhstan in the Shymkent city, was used. The tanning recipe for leathers is shown in Table I.

*Corresponding author email eser.eke@ege.edu.tr or eserekebay@gmail.com
Manuscript received June 22, 2023, accepted for publication October 18, 2023.

Table I

The recipe for leathers

Process	%	Product	Temperature	Time (min.)	pH
Washing	300	Water	30		
	0,3	Degreasing agent		60	
Drain & Wash					
	300	Water	35		
	2	Chromium salt			
	2	Synthetic tanning agent			
	2	Chrome syntan		60	
Neutralization	1	Sodium formate		60	
	2	Sodium bicarbonate		2×10+60	5,5-6,0
Drain & Wash					
Dyeing-fatliquoring-Retanning	150	Water	40		
	3	Dyestuff		35	
	+70	Water	70		
	6	Natural fatliquor agent			
	4	Synthetic fatliquor agent		60	
	3	Resin retanningagent		30	
	1	HCOOH		30	3,8-4,0
Drain & Wash					
Drying					

Two plants materials were used in this research during the finishing process: Oak bark (*Quercus cortex*) and Onion peel (*Allium cepa*), as shown in Table II.

Extraction Process

The plants were first dried and ground then 100 grams of dried plant material were mixed with 3000 grams of distilled water and boiled for 3 hours over low heat. The resulting liquid was cooled and filtered.[13,22]

Processes with Plant Extracts

During the finishing process of this recipe, a herbal extract made from oak bark (*Quercus cortex*), onion peel (*Allium cepa*), were used instead of chemical pigments. For the control sample, the basic finishing recipe with the use of a chemical pigment or water were used.

The recipe for the finishing of the leather is shown in Table III.

Table II

The plants used in the study and picking regions.

Plant type		Picking Regions	Extract's pH
Common Name	Botanical Name		
Oak bark	*Quercus cortex*	Kazakhstan	3,5
Onion peel	*Allium cepa*	Kazakhstan	4,5

Table III

Recipe for finishing process.

CHEMICALS	APPLICATION Coat (gramme)	EXPLANATIONS
Stage 1		
CPT 2350	150	Acrylic Binder (Alpa Chemistry)
CPT 2345	150	Binder (Alpa Chemistry) Acrylic Polymer
CPU 1641	150	Polyurethane Binder (Stahl)
CRE 1036	200	Acrylic Binder (Alpa Chemistry)
CST 6760	200	StukoWax (Alpa Chemistry)
CW 171	50	Synthetic Wax (Alpa Chemistry)
CW 159	50	StukoWax (Stahl)
CST HD	50	Polyurethane Binder (Stahl)
Dyestuff	2000	Plant Extracts (oak bark, onion peel) or chemical pigment
1) 3× spray – RotoPress (80°C, 150 Bar)-3× spray – RotoPress (80°C, 70 Bar)-3× spray (80°C, 70 Bar)		
Stage 2		
CK 1622	150	Polyurethane lacs (Stahl)
Dyestuff	300	Plant Extracts (oak bark, onion peel) or chemical pigment
1) 2× spray – RotoPress (90°C – 70 Bar)		

All leathers were conditioned for reproducible testing in the laboratory under the same conditions (20 ± 2 °C 65 ± 2% RH).

Aging Process

In many studies, the aging process is implemented for 24 hours at 80°C, and the Cr (VI) amount which occurs in leather is identified. In this study, in addition to the aging condition mentioned, tougher conditions were instituted to facilitate different aging processes with new treatment regimes, in order to form a higher amount of Cr(VI) in the leather and more clearly examine the effect of using herbal extracts. Leathers were aged in a heat-adjustable UV cabinet (UV light of 254 nm) at 80°C and under UV for 24h and 72h periods and Cr (VI) formation was thus enabled in the sample leather. In order to conduct comparative analysis and determine how the herbal extracts influence Cr (VI) formation in leather, subsequent aging processes on the leather were evaluated. Also, in the control group, leather samples were tanned into finished products, with no treatment with any extracts, and were compared with other treated samples to determine significant experimental effects.

Chromium (VI) Analysis on Leather Samples

Cr (VI) analysis of leather samples was conducted at 540 nm with Shimadzu UV-1601 PC UV-Visible brand spectrophotometer according to the IUC 18 (EN ISO 17075) standard method. The analysis was repeated three times.

Statistical Evaluation

When evaluating the results of the study, statistical analysis used NCSS (Number Cruncher Statistical System) 2023, Statistical Software (NCSS LLC, Kaysville, Utah, USA), descriptive statistics (mean, standard deviation, median, frequency and ratio).

Between groups of abnormal distribution of parameters Kruskal Wallis, Post HocDunn tests were used to identify differences between groups; Mann Whitney U test was used in the evaluation according to two groups. The results were evaluated at 95% confidence interval and $p<0.05$; $p<0,01$ significance levels.

Results and Discussions

In this investigation, onion peel and oak bark extracts were used in the finishing process. In the control groups, instead of these two extracts, the processes were carried out by using normal pigment in the factory or just water. After the finishing process, all leathers were conditioned for reproducible testing in the laboratory under the same conditions (20 ± 2 °C & 65 ± 2% RH).

In this study, Chromium(VI) content of leather samples after aging process (80 °C, 24h) is shown in Table IV.

Table IV

Chromium (VI) content of leather samples after aging process (80°C, 24h)

Type of sample	Cr (VI) mg/kg
control group	
chemical pigment 1	12.6
chemical pigment2	12.6
chemical pigment 3	12.6
water 1	12.07
water 2	12.1
water 3	12.01
experimental group	
oak bark 1	< 3
oak bark 2	< 3
oak bark 3	< 3
onion peel 1	< 3
onion peel 2	< 3
onion peel 3	< 3

Table V

Evaluation of chromium (VI) analysis measurements (80°C, 24h)

		Cr (VI) mg/kg
Control	Median (min-max)	12.3 (12.0 -12.6)
	Ort+SD	12.3±0.29
Experimental	Median (min-max)	2.0 (2.0-2.1)
	Ort+SD	2.05±0.05
Test Value		9.7
[c]p		0.007**
control group		
chemical pigment	Median (min-max)	12.6 (12.6-12.6)
	Ort+SD	12.6±0
water	Median (min-max)	12.1 (12.0-12.1)
	Ort+SD	12.1±0.01
experimental group		
oak bark	Median (min-max)	2.0 (2.0-2.0)
	Ort+SD	2.0±0
onion peel	Median (min-max)	2.0 (2.0-2.1)
	Ort+SD	2.05±0.05
Test Value		17
[e]p		0.004**
Post Hoc		oak bark - onion peel p:0.007** water - oak bark p:0.022*

[c]MannWhitney U test [e]Kruskal Wallis &Post HocDunn test *p<0.05 **p<0.01

Statistical evaluation of chromium (VI) analysis measurements (80°C, 24h) is shown in Table V.

When the research results are examined, a statistically significant difference between control group and experimental group was identified; chromium (VI) contents ($p < 0.05$); 12.3mg/kg Cr (VI) in control group, <3 mg/kg Cr (VI) in experimental group. In our study, a statistically significant difference was found between the chromium (VI) contents of chemical pigment and oak bark ($p < 0.05$); chemical pigment -12.6 mg/kg, oak bark <3 mg/kg. The content of onion peel was significantly lower in the experimental group than that of chemical pigment. There was no significant difference between the content of oak bark and onion peel ($p<0,01$). The content of water was significantly higher in the control group than that of onion peel. There was a statistically significant difference between the content of water and oak bark.

It can be clearly seen in Figure 1 that Cr (VI) formation is considerably reduced in leathers treated with onion peel and oak bark extracts.

Chromium(VI) content of leather samples after aging process (80°C, 24h) is shown in Table VI.

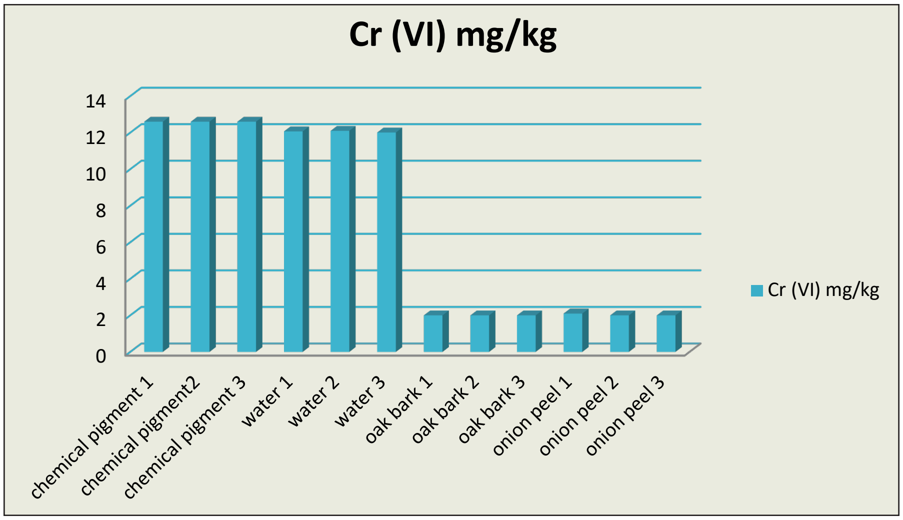

Figure 1. Chromium (VI) content of leather samples after aging process (80°C, 24h)

Table VI

Chromium(VI) content of leather samples after aging process by UV(80°C/UV, 24h).

Type of sample	Cr (VI) mg/kg
control group	
chemical pigment 1	13.2
chemical pigment 2	13.2
chemical pigment 3	13.2
water 1	12.4
water 2	12.4
water 3	12.4
experimental group	
oak bark 1	< 3
oak bark 2	< 3
oak bark 3	< 3
onion peel 1	< 3
onion peel 2	< 3
onion peel 3	< 3

Table VII
Evaluation of chromium (VI) analysis measurements(80 °C/UV, 24h).

		Cr (VI) mg/kg
Control	Median (min-max)	12.8(12.4-13.2)
	Ort+SD	12.8±0.4
Experimental	Median (min-max)	2.4(2.3-2.4)
	Ort+SD	2.35±0.05
Test Value		9.8
[c]p		0.008**
	control group	
chemical pigment	Median (min-max)	13.2(13.2 -13.2)
	Ort+SD	13.2±0
water	Median (min-max)	12.4(12.4-12.4)
	Ort+SD	12.4±0
	experimental group	
oak bark	Median (min-max)	2.3(2.3-2.3)
	Ort+SD	2.3±0
onion peel	Median (min-max)	2.4(2.4-2.4)
	Ort+SD	2.4±0
Test Value		17
[e]p		0.004**
Post Hoc		oak bark - onion peel p:0.007**
		water - oak bark p:0.022*

[c]MannWhitney U test [e]Kruskal Wallis &Post HocDunn test *p<0.05 **p<0.01

Evaluation of chromium (VI) analysis measurements(80°C/UV, 24h) is shown in Table VII.

No significant difference was found between chromium (VI) content after aging at 80°C, 24h and chromium (VI) after aging at 80°C/UV, 24h. The use of chemical pigment found the highest chromium (VI) content in the control group(p<0.05), chemical pigment – 13.2 mg/kg and water – 12.4 mg/kg.

Chromium (VI) obtained by using onion peel was found to be significantly lower than chemical pigment (p<0.05). No significant difference was found between oak bark and onion peel; oak bark

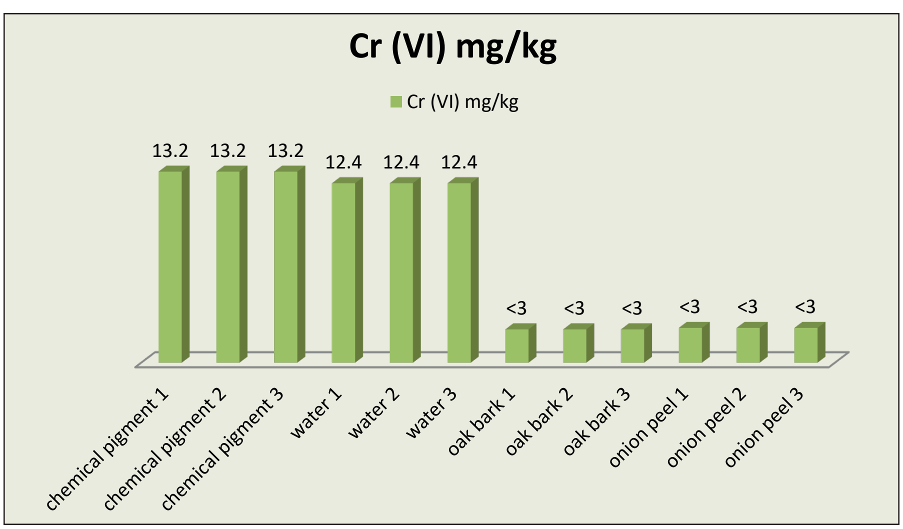

Figure 2. Chromium(VI) content of leather samples after aging process (80°C/UV, 24h)

<3mg/kg and onion peel <3 mg/kg (p<0.01). Figure 2 shows that the first six samples finished with the chemical pigment and water are significantly higher, the last six samples finished with the herbal extracts show that the amount of chromium (VI) decreased sharply.

Chromium(VI) content of leather samples after aging process (80°C/UV, 72h) is shown in Table VIII.

Evaluation of chromium (VI) analysis measurements (80°C/UV, 72h) is shown in Table IX. Chromium(VI) content in leather samples after aging process (80°C/UV, 72h)is shown in Figure 3. In this figure, a statistically significant difference was found between chromium (VI) content in the control and experimental groups.

Table VIII

Chromium(VI) content of leather samples after aging process (80°C/UV, 72h).

Type of sample	Cr (VI) mg/kg
control group	
chemical pigment 1	14.4
chemical pigment 2	14.4
chemical pigment 3	14.4
water 1	12.9
water 2	12.9
water 3	12.9
experimental group	
oak bark 1	< 3
oak bark 2	< 3
oak bark 3	< 3
onion peel 1	< 3
onion peel 2	< 3
onion peel 3	< 3

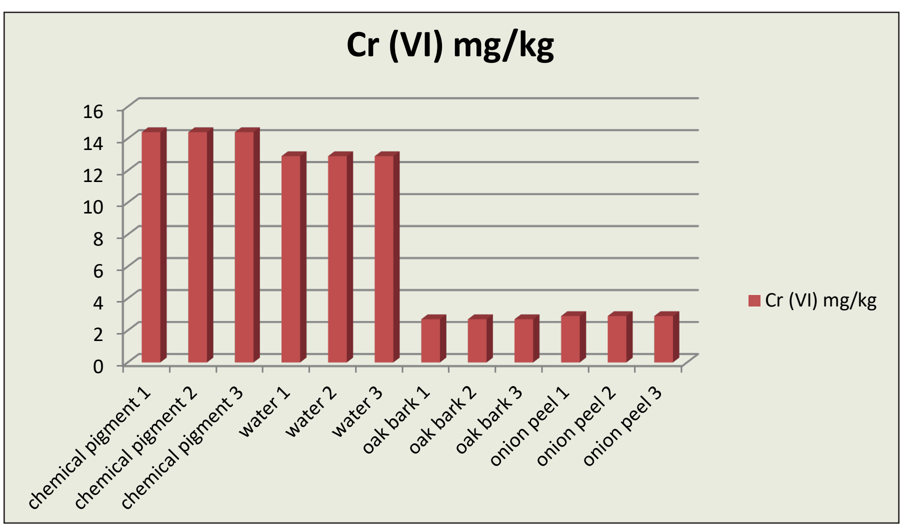

Figure 3. Chromium(VI) content of leather samples after aging process (80°C/UV, 72h)

Table IX

Evaluation of chromium (VI) analysis measurements(80°C/UV, 72h).

		Cr (VI) mg/kg
Control	Median (min-max)	13.6(12.9-14.4)
	Ort+SD	13.6±0.8
Experimental	Median (min-max)	2.8(2.7-2.9)
	Ort+SD	2.8±0.1
Test Value		2.7
[c]p		0.007**
control group		
chemical pigment	Median (min-max)	14.4(14.4-14.4)
	Ort+SD	14.4±0
water	Median (min-max)	12.9(12.9-12.9)
	Ort+SD	12.9±0
experimental group		
oak bark	Median (min-max)	2.7(2.7-2.7)
	Ort+SD	2.7±0
onion peel	Median (min-max)	2.9(2.9-2.9)
	Ort+SD	2.9±0
Test Value		17
[e]p		0.004**
Post Hoc		oak bark - onion peel p:0.007**
		water - oak bark p:0.022*

[c]Mann Whitney U test [e]Kruskal Wallis &Post Hoc Dunn test *$p<0.05$ **$p<0.01$

In this study, a statistically significant difference was found between chromium (VI) content in the control and experimental groups ($p <0.05$); chemical pigment was significantly higher in the control group, chromium (VI) content in the control group was 13.6 mg/kg; chromium (VI) content in the experimental group was <3 mg/kg. Chromium (VI) content obtained using onion peel was significantly lower than using chemical pigment($p<0.05$). A dramatically significant difference was found between chemical pigment and oak bark ($p <0.05$). No significant difference was found between oak bark and onion peel($p<0.01$), chromium(VI) content in oak bark was <3 mg/kg, chromium (VI) content in onion peel was <3 mg/kg.

A statistically significant difference was found between water and oak bark ($p<0.05$). Onion peel content was significantly lower in the experimental group than water.

Conclusion

In this study, the possibility of using some plant extracts as dyes in the finishing process of the leather was investigated. The recipe was provided according to the finished formula, replacing the chemical pigment and water with plant extracts such as oak bark and onion peel. For this reason, chrome-tanned crust leathers were dyed in the finishing process. These processes were repeated 3 times and compared with the leather control, which was made according to the main recipe, where the chemical pigment and water were used.

Three types of aging processes were carried out for the leather:1) the aging process was implemented for 24 hours at 80°C; 2) leather was aged in a heat-adjustable UV cabinet (UV light of 254 nm) at 80°C and under UV for 24h and 72 h periods and chromium (VI) formation was thus activated in the leather sample; 3) leather was aged in a UV cabinet (UV light of 254 nm) at 80°C and under UV for 72h period. In three cases, it was noticeable that chromium(VI) was significantly reduced in leather treated with natural extracts. In the first case, chromium (VI) in the chemical pigment trial showed 12.6 mg/kg; water 12.1 mg/kg; oak bark <3 mg/kg; onion peel < 3 mg/kg. In the second case, chromium(VI) in the chemical pigment 13.2 mg/kg; chromium(VI) in water 12.4 mg/kg; chromium(VI) in oak bark < 3mg/kg; chromium(VI) in onion peel < 3 mg/kg. In the third case, chromium(VI) in the chemical pigment– 14.4 mg/kg; chromium(VI) in water 12.9 mg/kg;chromium(VI) inoak bark < 3 mg/kg; chromium(VI) in onion peel < 3 mg/kg.

On this basis, it can be concluded that onion peel and oak bark extracts are able to reduce heavy metal like chromium (VI) in leather and are recommended to be used in the finishing process of leather. We believe that, this study represents is one of the most important research projects for the leather industry.

Acknowledgment

The authors express their gratitude to the Department of Leather Technology, Ege University and Deniz Kalender for her help in the lab and to "Turan-Skin" company that provided necessary resources for the study execution.

References

1. Hedberg, Y.S., Liden, C., Wallinder, I.O., Correlation between bulk- and surface chemistry of Cr-tanned leather and the release of Cr (III) and Cr (VI), *Journal of Hazardous Materials*, **280**, 654-661, 2014.
2. Covington AD., Tanning Chemistry, The Science of Leather. The University of Northampton, Northampton, 2009.
3. Fuck, W. F., Gutterres, M., Marcilio, N. R, et al., The influence of chromium supplied by tanning and wet finishing processes on the formation of Cr (VI) in leather, *Brazilian Journal of Chemical Engineering*, **28**, 221-228, 2011.
4. Kolomaznik, K., Adamek, M., Andel, I., et al., Leather waste-potential threat to human health and new technology of its treatment, *Journal of Hazardous Materials*, **160**, 514-520, 2008.
5. European Commission. Commission Regulation (EU) No 301/2014 amending Annex XVII to Regulation (EC) No 1907/2006 of the European Parliament and of the Council on the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) as regards chromium VI compounds [EB/OL].: European Commission, 2014-03-25.
6. Covington, A.D., Tanning Chemistry The Science of Leather, RSC Publishing, U.K., 2009.
7. Palpo, R., Parareda, J., Ballus, O., Leather aging and hexavalent chromium formation as a function of the fatliquoring agent. part II, chrome retanned leathers, *JSLTC*, **92**, 233-237, 2008.
8. Yu, C.Z., Sun, G.X., Guo, S.W., Exploration on the causes of Cr(VI) in leather, *China Leather*, **31**, 25-29, 2002.
9. Graf, D., Boehme, D., The influence of the relative humidity of air during storage on the formation lowering of Cr (VI) in chrome tanned leather, World Leather, **13**, 38, 2000.
10. Yu, C.Z., Liu, P.J., Sun, G.X, et al., The influence of relative humidity on the level of Cr (VI) in chrome-tanned leather, *JSLTC*, **89**, 194-198, 2005.
11. Bayramoğlu, E.E., Soaking with Storax – Possibility of Using SiğlaTree (Liquidambar orientalis Mill. varorientalis) Storax as Bactericide in the Soaking Float, *JALCA*, **105**, 2010.
12. Bayramoğlu, E.E., Bayram S.E., Alternative Natural Deliming Agents, *Journal of AQEIC,* **64** (1), 2013
13. Bayramoğlu, E.E., Korgan, A., Kalender, D., Gülümser, G., Okçu, B. and Kılıç, E., Elimination of Free Formaldehyde in Leather by Vincarosea and Camellia sinensis. *JALCA*, **103**(3), 119-123, 2008.
14. Bayramoğlu, E.E., Unique Biocide for the Leather Industry: Essential Oil of Oregano, *JALCA*, **102**(11), 347-353, 2007
15. Bayramoğlu, E.E, Gülümser, G., Karaboz, İ., Ecological and Innovative Fungicide for Leather Industry: Essential Oil of Origanum multiflorum, *JALCA*, **101**(3),96-104, 2006.
16. Çolak, S., Bayramoğlu, E.E, Uluç, D., Determining the Usability of Photosensitizers as Biocides in Soaking Process, *JALCA*, **101**(2), 66-72, 2006.
17. Bayramoğlu, E.E.E, Antibacterial Activity of Myrtus communis Essential Oil Used in Soaking, *JSLTC*, **90**,Number 5, 2006.
18. Bayramoğlu, E.E, Gülümser, G., Karaboz, İ., The Investigation of Antibacterial Activities of Some Essential Oils in Wet Blue Leather, *IJNES*, **2**(1):33-36, 2008.
19. Bayramoğlu, E.E, Natural and Environment Friendly New Bactericide for Leather – Industry: Essential Oil of Origanum multiflorum, Ansinet, *Journal of Biological Sciences,* **5**(4) 455-457, 2005.
20. Bayramoğlu, E.E., Hidden Treasure of the Nature:Pas, The Effects of Grape Seeds on Free Formaldehyde of Leather, *Industrial Crops and Products*, **41**, 53-56, 2013.
21. Yu, C.Z., Wang, R., Ma, X.Y., et al.; Antioxidant effect of phenolic compounds on unsaturated lipids preventing the oxidation of chromium (III), *JSLTC*, **94**, 33-38, 2010.
22. Bayramoğlu E.E., Leather Technology Lesson Notes, 2023 (Unpublished).