(REFEREED RESEARCH)

FLAME RETARDANT EFFECT OF TRI BUTYL PHOSPHATE (TBP) IN VEGETABLE TANNED LEATHERS

BİTKİSEL TABAKLANMIŞ DERİLERDE TRİ BÜTİL FOSFATIN (TBP) ALEV GECİKTİRİCİ ETKİSİ

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ABSTRACT

Tributyl Phosphate (TBP) is classified as organophosphorus compounds and shows a fire retardant effect in different material. In this work, lime splitting cattle leathers was tanned two type vegetable tannings, Mimosa (Group 1) and Tara (Group 2) and then TBP was applied to the non-finished vegetable tanned leathers at different concentrations. (0%, 7%, 14%, 21%) After the flame retardant mixture applied to the vegetable tanned leathers, samples were finished with a standard finishing recipe. Fire retardant effect on TBP treated leathers was determined by LOI test. Also morphological properties of leathers by SEM, molecular binding characterization of leathers by ATR-FTIR Analysis and color properties of leathers by CIE Lab Color Analysis were researched. The results showed that TBP treated vegetable tanned leathers were good flame retardant effect.

Keywords: Leather, Fire, Flame Retardant, Vegetable Tanned, Tributyl Phosphate

ÖZET

Organo fosforlu bileşikler sınıfında yer alan Tribütil Fosfat kimyasalı; farklı materyallerde alev geciktirici etki göstermektedir. Bu çalışmada; kireçlik yarması sığır deriler Mimoza (Grup 1) ve Tara (Grup 2) olmak üzere iki çeşit bitkisel tabaklayıcı ile tabaklanmıştır ve sonrasında (0%,7%, 14%, 21%) farklı konsantrasyonlarda finisajı yapılmamış bitkisel tabaklanmış derilere TBP uygulanmıştır. Bitkisel tabaklanmış derilere alev geciktirici karışım uygulandıktan sonra örnekler standart bir finisaj reçetesi ile mamul hale getirilmiştir. TBP ile iyileştirilmiş derilerin alev geciktirici etkisi LOI testi ile tanımlanmıştır. Ayrıca SEM ile derilerin morfolojik özellikleri, ATR-FTIR ile derilerin moleküler bağ karekterizasyonu ve CIE Lab Renk Analizi ile derilerin renk özellikleri araştırılmıştır. Sonuçlar TBP ile iyileştirilmiş bitkisel tabaklanmış derilerin iyi bir alev geciktirici etkiye sahip olduğunu göstermiştir.

Anahtar Kelimeler: Deri, Alev, Alev Geciktirici, Bitkisel Tabaklama, Tribütil Fosfat

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1. INTRODUCTION

There are several methods for tanning leather, but not all of them are the right choice for your health or environment. Chrome-tanning is the most popular and controversial, due to its widespread use in the fashion industry. But the use of chromium salts is harmful to the human and environmental health. Vegetable-tanning is the true "chromium-free" method, and does not have harmful chemicals [1]. In this way leather industry latterly have been increased to use vegetable tannins to be healthier than chrome tanned leathers. In vegetable tanning production, various types of vegetable tannins which are known as hydrolysis and condensation molecular structures, gives to the leathers different color tone (brown, red brown, yellow brown, red, etc.). Thus color and light fastness of the vegetable tanned leather can be affected according to their chemical properties [2,3]. The production of flame retardant leather is important for some leather types as motorcyclist jackets, flight or automotive upholstery leathers. If these type leathers ignite lately, the retardant property of material will provide gain in time to rescue humans and animals during the fire [4,5]. Flame retardants can have classifed as halogen containing flame retardants and halogen-free flame retardants. Phosphorus based flame retardant chemicals are one of these categories and there are many written work about the effects of flame retardants in literature. Tributyl Phosphate (TBP) is classified as organophosphorus compounds and shows a fire retardant effect in different materials [6,7,8]. Vegetable-tanned leathers contain more water ions than other leather types due to the hydroxyl groups present in the molecular structures. For this reason, it is known that Vegetable-tanned leathers burn more later than the other types of leather in the initial stage during fire [9,10,11]. In this study, it was aimed to increase the flame retardancy properties of vegetable tanned leathers with TBP. Furthermore, the effects of color fastness of TBP on the vegetable tanned leathers were also investigated.

2. MATERIAL AND METHOD

2.1 Material

Lime Splitting Cattle Leathers were supplied from Tuzla Leather Industrial Area. Tributyl Phosphate- TBP (97%) was obtained from Sigma (St. Louis, USA), 2-Propanol (≥99.5%) was obtained from Sigma (St. Louis, USA). In the finishing recipe; different chemicals were used, Sarpur 317 (Sarchem b.v.) as polyurethane binder, Saracryl 588 (Sarchem b.v.) as acrylic binder, Sarfill 8537 (Sarchem b.v.) as filler, Sarkol K Black (Sarchem b.v.) as black Pigment, Sarwaks 8147 (Sarchem b.v.) as wax, Selladerm Black (TFL Company) as anilin dye, Sartop 118 (Sarchem b.v.) as protein binder, Melio EW 348B (Clariant b.v.) as hydrolacque, Melio WF 5226 (Clariant b.v.) as feeling agent. In leather production recipe is used Bemanol DLFA (Stahl Company) as deliming chemical, Bemanol 5BN (Stahl Company) as pancreatic enzyme for bating process, Corilene HLG (Stahl Company) as fatliquoring agent, Synektan BEH (Stahl Company), Neutraktan D (Stahl Company) as neutralization chemical, Corilene N-60 (Stahl Company) as faliquoring agent, Salem GC (Stahl Company) as synthetic sulphited fatliquor for soft leathers, Corilene F-265 (Stahl Company) as naturel and synthetic sulphate fatliquor, mimosa extract (BASF Company) as hydrolyzed vegetable tannins, tara extract (BASF Company) as condensed vegetable tannins.

2.2 Method

Lime Splitting Cattle Leathers were produced as vegetable tanning methods and recipe of leathers was given in Table 1. In tanning process was divided two groups as mimosa and tara tannins. Mimosa was the condensed tannin group, having lower light fastness and tara was the hydrolyzed tannin, having good light fastness property. Vegetable tanned leathers did not make the finishing process before TBP application. Tributyl Phosphate-2-Propanol (TBP-IPA) mixtures were prepared at different concentrations for the flame retardant application. (0%, 7%, 14%, 21%).

Table 1. Recipe of Leather Process

Leather Process	Chemical Additives	T (ºC)	Rate (%)	Time (min)	Remarks
Weight					
Deliming	Water	35	200		
	(NH4)2SO4		0.3	60	pH 8
	Bemanol DLFA		3		
Bating	Bemanol 5BN	35	0,5	40	
Washing	Water	25	300	10	Drain
Pickle	Water	22	80		
	Common salt		8	10	7 ºBé
	HCOOH		1,6	(3X15min)+30	
	Corilene HLG		0,5	30	
	H_2SO_4		0,2	(3x10min)+90 min	pH:2.8
Tanning	Synektan BEH	22	1		
	Mimosa(Group1) Tara (Group 2)		5	30	
	Corilene N-60		0,5	60	
Washing	Water	25	30		Drain, 48 h horse up
Bleaching	Water	30	200		
	Funguside	20	0,3	20	
	EDTA		0,3		
	Oxalic Acid		1	60	Drain
Washing	Water	35	200	15	Drain
Neutralization	Water	35	150	15	
	Sodium formate		2		
	Neutraktan D		0,8	90	pH: 5-5.2, Drain
Washing	Water	20	200	15	Drain
Retanning	Water	20	50		
	Synektan BEH		2	15	
	Mimosa (Group 1) Tara (Group 2)		8		
	Corilene N-60		1	90	
Fatliquoring-1	Water	45	100		
	Salem GC		4		
	Corilene N-60		2		
	Corilene F-265		3	60	
	HCOOH		0,4	30	Drain
Washing	Water	45	200	15	Drain
Fatliquoring-2	Water	45	100		
	Salem GC		3		
	Corilene F-265	40	2		
	HCOOH	10	0,2		Drain
Washing	Water	20	200	15	
	EDTA		0,2		Drain

Also 0% group leather samples were only applied IPA solution for the homogenous application. Surface of leather samples were treated with TBP-IPA solutions by Leather Padding Technique which is a kind of finishing technique, made by hand and is used for the intense or decorative pattern finishing applications. All leathers were dried in the room temperature for 24 h and then same application was repeated once again. After the proposed flame retardant mixture applied, samples were finished with a standard finishing recipe. (Table 2.)

Table 2. Finishing Recipe of TBP Applied Leathers

Chemical	Rate	Finishing Application
Polyurethane Binder (g)	100	2x Spray Press (70 atm, 90 °C,1sn) 1 x Spray Press (70 atm, 90 °C,1sn)
Acrylic Binder (g)	100	
Protein Binder (g)	25	
Filler (g)	35	
Casein Binder (g)	25	
Waks (g)	30	
Pigment Dye (g)	80	
Anilin Dye (g)	20	
Water (g)	500	
Hydrolaque (g)	100	1 x Spray Press (70 atm, 90°C, 1 sn)
Feeling Agent (g)	10	
Water (g)	150	

2.3 Measurements

Limit oxygen index (LOI) tests were performed on a limiting oxygen index chamber with strips of fabrics according to ASTM D 2863-77 [12]. 15 pieces leather samples for each group (140 mm x 60 mm) were taken from flame-retardant leather and were used for parallel tests. For SEM analysis the samples were placed on a scanning electron microscope (Fei-Quanta Feg 250) and their images were taken at 100 μm and 20 μm magnifications. FTIR analysis was conducted in order to determine the differences in the chemical properties of leather treated with TBP and control group (0%). FTIR studies were conducted on Bruker-Vertex70 ATR device with ATR equipment. For this purpose, the leather samples were scanned with IR spectrums at a wavelength of 4000-600 cm-1 and the results were evaluated in the FTIR Spectrum Software and compared with the spectrums in the literature. A Konica Minolta CM-508D brand global spectrophotometer with an 8 mm diameter measurement area was used in the measurement of the leather dyes. Measurements were taken from 10 different areas of each leathers according to CIE Lab (1976) and the color differences were determined between treated and untreated leathers in CIE 100 standard observer angle and CIE standard D65 light source. In the components of the CIE Lab color space, L* is the lightness of color, and a* and b* indicate the color. If L* has a negative value, it means that the color of sample has darkened, while if it has a positive value, it means that the sample color has turned lighter [13]. If a* has a negative, it means that the sample color has turned greener, and if it has a positive value, it means that the sample color has turned redder. If b* has a negative value, it means that the sample color has become bluer, and if it is positive, it means that the sample color has turned yellower. ΔL is difference darkness of lightness, Δa is difference redness and greenness and Δb is difference yellowness and blueness between samples and standard samples [14,15]. ΔE which is total color difference, is calculated below equation. (1)

ΔE= [(ΔL*)2+(Δa*)2+(Δb*)2]1/2 (1)

3. RESULTS

3.1 LOI Results

Limiting Oxygen Index (LOI) which is probably the most well-known of the standard fire tests and required specification for all type materials, is the per cent concentration of oxygen at a sample. LOI results of mimosa and tara vegetable tanned leathers were given in Table 3. According to the results, the LOI values of mimosa-tanned leathers were higher than tara-tanned leathers. While mimosa tanned leathers were increased from %39.2 to 39.7; tara tanned leather were raised from %33.1 to %34.1. %7 and %14 TBP rates did not show flame retardant effect both types of leathers. In addition, LOI values in all groups were higher than other natural polymers or textiles such as wool, cotton, silk because of their high hydrophilic hydroxyl groups in the molecular structure of vegetable tannins. In other words, their burning behavior of leathers have delayed because of the moisture or water.

Table 3. LOI Results of TBP Treated Vegetable Tanned Leathers

Group	LOI (%)
Mimosa	
0%	39.2
7%	39.2
14%	39.2
21%	39.7
Tara	
0%	33.1
7%	33.1
14%	33.1
21%	34.9

3.2 CIE Lab Results

Table 4 shows the results of CIE Lab after TBP was applied to vegetable tanned leathers in different concentration. Since the vegetable tannins used in leather production give their own colors to the leathers, there are problems in adjusting the color tone of the leathers during the dying process. For this reason, it is important to bleach the leather or lightness the color to obtain the desired color [16]. From this point of view, ΔL values was increased 2 unit after TBP application to the mimosa tanned vegetable leathers.

Δa values, being redness and greenness, was changed from 0.06 to -0.96. It is mean that greenness effect of mimosa tanned vegetable leathers was raised by TBP effect. Δb values, being yellowness and blueness, was observed -2 unit decreasing and the blue color of mimosa tanned vegetable leathers was increased by TBP. When CIE Lab values of tara tanned leathers was examined; it was seen that ΔL values was increased from -0.17 to 1.39. Δa values was changed negative direction by TBP and was decreased from -0.26 to -2.64 in tara tanned vegetable leathers. Similarly, Δb values was changed negative direction by TBP and was decreased from -3.13 to -5.58 in tara tanned vegetable leathers. When it is compared both mimosa and tara tanned vegetable leathers; TBP shows lightness effect better result than mimosa tanned leathers. This difference can be related with molecular structure of tannins, being hydrolysis or condense.

Table 4. CIE Lab Results of TBP Treated Vegetable Tanned Leathers

Group	L*(D65)	a*(D65)	b*(D65)	ΔL	Δa	Δb	ΔE
Mimosa							
%0	50.03	23.78	25.78				
%7	52.9	23.84	24.09	2.87	0.06	-1.69	3.33
%14	52.2	23.32	22.7	2.17	-0.46	-3.71	4.32
%21	52.37	22.82	21.79	2.34	-0.96	-3.99	4.72
Tara							
%0	66.39	16.04	52.28				
%7	66.22	15.78	49.15	-0.17	-0.26	-3.13	3.14
%14	65.38	15.25	46.91	-1.01	-0.79	-5.37	5.52
%21	67.78	13.4	46.7	1.39	-2.64	-5.58	6.32

3.3 ATR-FTIR Results

ATR-FTIR Results of mimosa and tara tanned vegetable leathers were given in Figure 1. According to results of TBP treated mimosa tanned vegetable leathers, FTIR spectrums shows 3300 cm^{-1}, 2923 cm^{-1}, 2850 cm^{-1}, 1730 cm^{-1}, 1643 cm^{-1}, 1540 cm^{-1}, 1377 cm-1, 1449 cm^{-1}, 1277 cm^{-1}, 1027 cm^{-1}, 838 cm^{-1}, 536 cm^{-1}. The mimosa condensed tannin gave at 1277 cm^{-1} C-O stretching of flavonoid pyran. Hydroxyl groups appeared in 3284 cm^{-1} and 1377 cm^{-1} peaks which are coming from tannin extract and leather molecular structure [17]. The region of 2923 cm^{-1} is related the CH, CH_2, and CH_3 stretching vibrations which are occurred because of leather structure or carbohydrates and sugars derivates of tannin [18,19]. The stretching of the C=C-C aromatic bond appeared in the region of 1643-1449 cm^{-1} which is based on aromatic structure of vegetable tannins [20].

According to results of TBP treated tara tanned vegetable leathers, FTIR spectrums shows 3284 cm^{-1}, 2917 cm^{-1},2850 cm^{-1},1728 cm^{-1},1650 cm^{-1}, 1540 cm^{-1} , 1448 cm^{-1} ,1377 cm^{-1}, 1279 cm^{-1}, 1161 cm^{-1}, 1027 cm^{-1}, 907 cm^{-1}, 841 cm^{-1}. Tara is a hydrolysed tannin which is from gallo tannins class and in this way 1728 cm-1 peak showed the C=O stretching of esters of hydrolysable tannins, derivatives of gallic acid [21]. However %21 TBP treated mimosa and tara tanned vegetable leathers gave strong stretch P=O in 1320-1140 cm^{-1} peaks because of phosphate compounds of TBP [22].

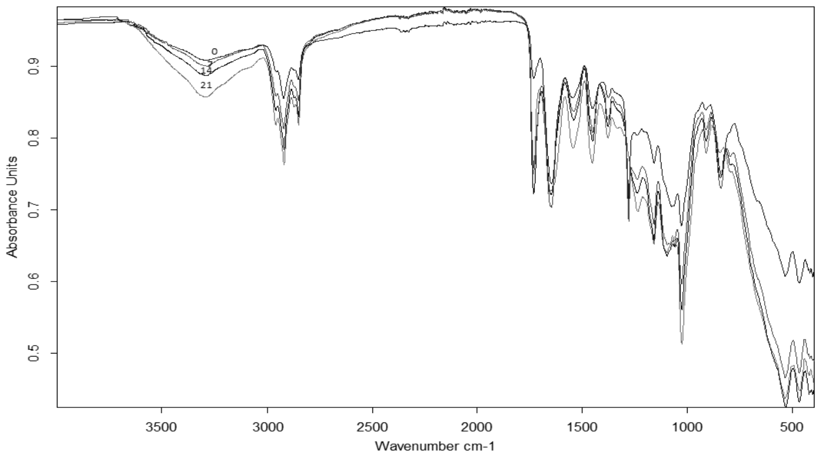

Figure 1. ATR-FTIR Results of Mimosa Tanned Vegetable Leathers

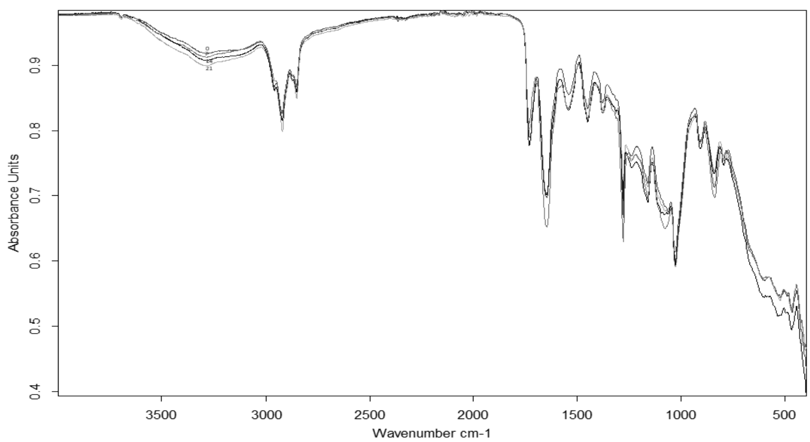

Figure 2. ATR-FTIR Results of Tara Tanned Vegetable Leathers

3.4 SEM Results

SEM images 100 µm and 20 µm magnifications of TBP treated mimosa and tara tanned leathers after finishing application is given in Figure 3 and Figure 4. These images show that in 0%, 7% and 14% TBP applied mimosa and tara vegetable tanned leather samples have not observed significantly changing and the deformations on the surfaces of the leathers are similarly same. So TBP showed that it does not cause damage problems in these application rates for the leathers and it can be used easily for vegetable leathers.

4. CONCLUSIONS

In this work, the color effect and of TBP in surface of mimosa and tara vegetable tanned leathers were studied. After TBP application while mimosa tanned leather was appeared %39.7 LOI result in %21 TBP, tara tanned leathers gave %34.9 LOI value in %21 TBP. In this way; TBP chemical increased the flame retardant property of vegetable leathers. However interesting result was obtained in CIE Lab and ΔL values were increased in the mimosa and tara vegetable leathers by TBP application. In SEM results; TBP applied vegetable leather samples have not observed significantly changing and harmful effect on the surfaces of the leathers were seen similarly same. As a result, TBP chemical can be used reliably in mimosa and tara vegetable tanned leathers in order to obtain flame retardancy.

5. ACKNOWLEDGMENT

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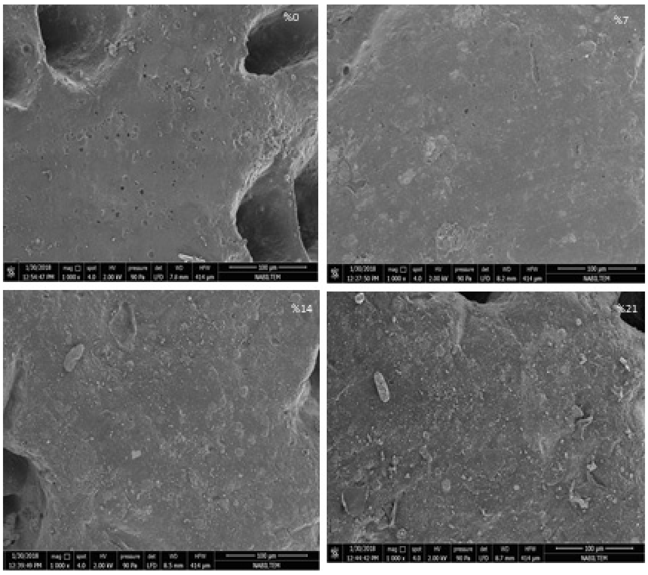

Figure 3. SEM Results of TBP Applied and Mimosa Tanned Vegetable Leathers in 100 µm

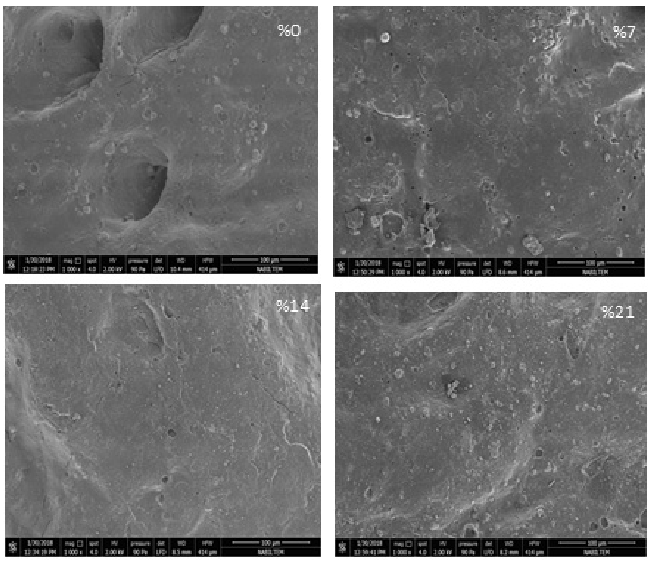

Figure 4. SEM Results of TBP Applied and Tara Tanned Vegetable Leathers in 100 µm

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