

MODIFICATION OF MIMOSA AND QUEBRACHO TANNINS AND THE LIGHTFASTNESS PROPERTIES OF THE PROCESSED LEATHERS

MİMOZA VE KEBRAKO TANENLERİNİN MODİFİKASYONU VE ÜRETİLEN DERİLERİN IŞIK HASLIĞI ÖZELLİKLERİ

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ABSTRACT

Vegetable tannins give leathers some properties like natural look, firmness, toughness and characteristic colour of themselves. Besides these favourable properties, some of the tannins as mimosa and quebracho which belong to condensed tannins, have some undesirable properties like colour changing and darkening caused by exposure to light for prolonged times. This research aims to increase the lightfastness properties of mimosa and quebracho tanned leathers, by chemical modification of these tannins. For this aim sulphitation, sulpho methylation and novalac synthesis modifications were applied to mimosa and quebracho tannins. Comparative lightfastness test results showed that leathers tanned with sulpho methylated mimosa and quebracho tannins had better fastness to light. Additionally the physical properties of the leathers tanned with modified tannins were investigated to compare with the leathers tanned with standard tannins.

Keywords: Vegetable Tanning, Mimosa, Quebracho, Lightfastness, Leather

ÖZET

Bitkisel tanenler deriye doğal bir görünüm, dolgunluk, sıklık ve tanenin kendine has renk tonu gibi özellikler kazandırır. Bu olumlu özelliklerin yanında kondanse tanen grubunda yer alan mimoza ve kebrako tanenlerinin, UV ışığına maruz kaldıklarında renk değiştirme ve kararırma gibi olumsuz özellikleri bulunmaktadır. Bu araştırma, tanenlerin kimyasal olarak modifikasyonu ile, mimoza ve kebrako ile tabaklanan derilerin ışık haslığı özelliklerini artırmayı amaçlamaktadır. Bu amaçla mimoza ve kebrako tanenlerine, sülfütasyon, sülfometilasyon ve novalak sentezi modifikasyonları uygulanmıştır. Karşılaştırmalı ışık haslığı ölçüm testleri göstermiştir ki sülfometilasyon uygulanmış mimoza ve kebrako ile tabaklanan deriler daha iyi bir ışık haslığına sahiptir. Bu çalışmada ayrıca modifiye tanenlerle tabaklanmış derilere ait fiziksel özellikler de belirlenmiş ve standart tabaklama referansları ile karşılaştırılmıştır.

Anahtar Kelimeler: Bitkisel Tabaklama, Mimoza, Kebrako, Işık Haslığı, Deri

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INTRODUCTION

Vegetable tanning materials have been used from the ancient times of human history and they have still importance in today's leather processing due to their natural look and feel that give to leathers and being eco-friendly. Vegetable tannins have polyphenolic structure and they usually give a tight and full character to leather. They are preferred in production of sole leathers, shoe uppers, upholstery leathers and leather goods because of their

specific character. Not only these tannins give favourable properties to leather but also they are more or less sensitive to light and they have the disadvantage of colour changing by exposure to light with time.

Colour fading is a photochemical incident. The light falling on an object can be reflected or absorbed; if the light energy which has effective role on fading is absorbed by the material it can transform to heat or can cause some chemical reactions in the object (Gulumser et al., 2008).

Sunlight is reaching to earth as electromagnetic radiation. The spectral form and intensity of light exposed on a dyed material have great effect on fading degree. The radiation between 290-400 nm is named as Ultra violet or UV. This radiation up to 400nm have more energy and can break ionic, hydrogen and even covalent bonds (Oktem vd., 2008).

According to Pizii et al., (2004), the variation of leather colour as a function of ageing time on prolonged irradiation with UV light of the leather produced based on different vegetable tannins was found to be composed of two main effects: The first one of these is the darkening reaction of the leather. This is due to the formation of quinones on the phenolic structure of the vegetable tannin. The second one is the leather-lightening (fading) reaction due to the photo degradation of the system.

For Covington, (2009) the ability of phenols to discolour (in the case of vegetable tannins, the darkening effect is to redden) depends on the formation of phenyl radicals by the loss of hydrogen to atmospheric oxygen. The free radical formation causes bond shifts and oxidative coupling, which means polymerisation: if this results in the creation or the linking of chromophoric groups then colour is developed. In the case of the hydrolysable tannins, the chromophores, the benzene rings of the ester moieties, are not linkable because they are too far apart in the molecule: in this way they are resistant to reddening, referred to as lightfast. In the case of the condensed tannins, the proximity of the aromatic nuclei in the flavonoid structure means that the free radical oxidative bond rearrangements can take place easily. Therefore, these tannins redden, creating a rapid colour change on the leather surface.

Hence in this research, sulphitation, sulpho methylation and novalac synthesis modifications were applied to mimosa and quebracho tannins to introduce UV stabile groups to their flavonoid structure to avoid free radical oxidative bond rearrangements. The modified tannins were used in leather production. Then their physical and lightfastness properties were measured and compared with the leathers tanned with standard mimosa and quebracho.

EXPERIMENTAL

1.1. Material

10 pickled whole domestic hides each weighing approximately 10 kg, at pH 2.5 were used as the raw material for vegetable tanning. The thicknesses of pickled hides were adjusted to 1.4 mm for better and homogenous penetration of tannins and chemicals.

Mimosa and quebracho tannins were used from the condensed tannins group due to their lower light fastness properties considering the pre trials, literature and studies of Ozgunay (2008), Pizzi et al, (2004), Frediani et al. (2008). Mimosa and quebracho tannins were obtained from Mimosa Extract Company (Pty).

Phenolsulphonic acid, urea, formaldehyde, sodium sulphide at analytic grade (purchased from Merck) and a commercial UV stabiliser containing Hindered Amine Light Stabilizers (HALS) (purchased from BASF) were used in modification experiments.

1.2. Method

1.2.1. Modification Procedure

In this research standard, sulphomethylated, novalac type modified, sulphitated mimosa and quebracho were encoded as M0, K0, M1, K1, M2, K2, M3 and K3 respectively. Modification procedures are given below.

Sulphomethylation

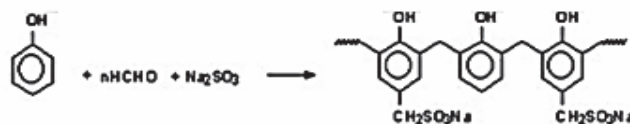


Figure 2. Sulphomethylation of phenols (Frediani et al., 2008)

Sulphomethylation reaction occurs by the binding of sulphomethyl group (-CH₂-SO₃R), to the amine and amide compounds. This reaction has been widely used in urea and melamine based amino resin synthesis (Kasgoz, 1999). Mimosa tannin was sulphomethylated by this procedure (Frediani et al, 2008).

In this modification 30% mimosa and quebracho tannins based on pelt weight were dissolved in beakers. The temperature was set to 70 °C. Then the tannins were modified with 8% sodium sulphide and 8% formaldehyde addition based on tannin weight.

Novalac synthesis

This modification process of mimosa and quebracho tannins was based on the process given by Covington (2009).

In this modification, 30% mimosa and quebracho tannins based on pelt weight were dissolved in beakers. 20% phenol sulfonic acid, 1.5% urea and 5.5% formaldehyde based on tannin weight were added and the temperature was set to 75 °C. Then the modification was completed by addition of 12.5% sodium sulphide.

Sulphitation

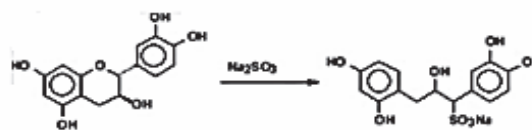


Figure 3. The sulphitation of monomeric form of catechins (Frediani et al., 2008)

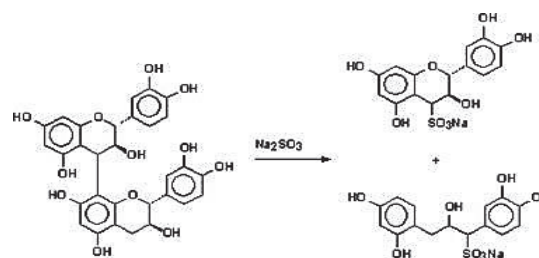


Figure 4. The sulphitation of dimeric form of catechins (Frediani et al., 2008)

This modification procedure was based on the literature of Frediani et al., (2008). In the modification process the solvent free HALS compound was used. This compound is a dispersion that can be used in water based systems and prevents breaking, powdering and discolouring of coatings by preventing photo oxidation of binders.

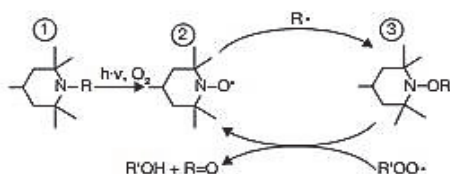


Figure 5. Chemical structure of UVS-HALS compound

In this modification 30% mimosa and quebracho tannins based on pelt weight were dissolved in beakers. 12.5% Sodium sulphide based on tannin weight was added and the temperature was set to 70 °C. Then the modification was completed by addition of 5% UVS-HALS.

1.2.2. Tanning Process

Before vegetable tanning the pH value of pickled pelts were adjusted to pH 5.5 by depickling process (Table 1).

The hides were tanned by using the vegetable tanning process illustrated in Table 2. Then the leathers were dried in a dark place and mechanical processes like milling and toggling were carried out.

Table 1. Depickle Process

Material	Pickled hide	Temperature	Time
Weighting	Pickle weight + 20%		
Depickle	200% Water 8 °Be	30 °C	15 min.
	1.2% Sodium formate		30 min.
	2% Sodium bicarbonate		240 min.
Draining			pH=5,5
Washing	200% Water	30 °C	20 min.
Draining			

Table 2. Vegetable Tanning Recipe

Material	Pickled Hide	Temperature	Time
Weighting	Pickle weight + 20%		
Vegetable Tanning	200% Water	30°C	
	2% Lightfast Syntan		30min
	10% Tannin		
	1% Lightfast synthetic fatliquor		20min
	20% Tannin		60min
	60% Water	55°C	10 min
	6% Lightfast synthetic fatliquor		300min
Fixation	1.5% Formic Acid (1/10 Diluted)		240 min
Draining			pH=3.8
Fixation	300% Water	50°C	
	0.3% Formic Acid (1/10 Diluted)		30min
Draining	150% Water	50°C	15min
Rinsing	300% Water	25°C	20 min

1.2.3. Physical and Instrumental Analysis of Tanned Leathers

The resulting leather samples were placed in Alpha+ Xenotest light fastness measuring instrument and light fastness was determined by exposing to light according to standard TS EN ISO 105-B02, 2014. Colour measurements were made by using Minolta 508d colour spectrophotometer.

The physical tests were carried out by using TS ISO standards. Then the tests were performed on leather samples prepared as reported by the TS EN ISO 2418 (2006) and TS EN ISO 2419 (2012) standards. The tests and related standards used in the research are listed below:

- Determination of the thickness, TS 4117 EN ISO 2589 (2006)
- Determination of shrinkage temperature, TS 4120 EN ISO 3380 (2005).
- Determination of the tensile strength and percentage elongation, TS 4119 EN ISO 3376 (2012)
- Determination of tear load, TS 4118-1 EN ISO 3377-1 (2012)
- Determination of distension and strength of grain by Ball Burst, TS 4131 (1985)
- Determination of colour fastness of leather to light: Xenon lamp, TS EN ISO 105-B02 (2014)
- Determination of colour change, TS 423-5 EN ISO 105-A05 (2001).
- Determination of free and released formaldehyde in leathers, TS EN ISO 17226-1, (2009).

1.2.4. Statistical Methods

Outputs were statistically analysed to find out the significant differences between the means. For the stated purpose ANOVA, descriptive statistical test and Duncan test were carried out by using statistical software package (SPSS version 16.0). Besides this the 0.05 significance level was selected for the tests. (Elliott and Woodward, 2007).

RESULTS AND DISCUSSION

The results of colour measurements and colour differences (dE) of standard and modified mimosa and quebracho tanned leathers before and after artificial light exposure are illustrated in Table 3 and Table 4 in CIE Lab coordinates.

According to the results in Table 3 and Table 4, the lowest colour changes are observed from the leathers which were tanned with sulphomethylated mimosa and quebracho tannins (M1 and K1). With the statistical evaluation of these results, it shows that there are significant differences among the values ($p=0,001$ and $p=0,013$). As a result, sulphometilation modification is the best process for decreasing the colour changing effect of UV light on mimosa and quebracho tannins among other modification trials tested in this study.

Afterwards physical tests were applied to sulphomethylated mimosa and quebracho tanned leathers and the results were compared with standard mimosa and quebracho tanned leathers. And physical test results of leathers tanned with standard and sulphomethylated mimosa and quebracho tannins are illustrated in Table 5.

Table 3. Colour Change Measurements of Leathers Tanned with Non-Modified and Modified Mimosa Tannins

Leather Sample	L	Before		L	After		dE
		a	b		a	b	
M ₀	69,42	8,28	12,21	55,85	17,18	29,51	23,72
M ₁	46,24	12,25	18,35	42,47	17,94	25,28	9,72
M ₂	64,28	12,74	19,51	46,59	20,46	29,90	21,91
M ₃	50,94	10,39	14,56	53,43	13,19	28,45	14,38

Table 4. Colour Change Measurements of Leathers Tanned with Non-Modified and Modified Quebracho Tannins

Leather Sample	L	Before		L	After		dE
		a	b		a	b	
K ₀	67,07	12,20	20,59	51,61	18,63	28,99	18,73
K ₁	45,77	13,53	19,8	43,1	20,7	27,93	11,16
K ₂	44,03	17,37	23,34	30,06	16,97	12,75	17,54
K ₃	63,63	12,30	21,71	51,84	19,27	29,76	15,89

Table 5. Physical Test Results of Leathers Tanned with Standard and Modified Mimosa and Quebracho Tannins

Leather Sample	Ts (°C)	Tensile strength (N/mm ²)	Elongation (%)	Tear load (N/mm)	Strength of grain (kgf)
M ₀	83,77	29,86	30,01	85,55	100
M ₁	92,23	19,87	31,46	65,78	96,5
K ₀	79,45	21,83	27,66	58,48	92,5
K ₁	83,85	20,24	31,48	78,15	100

According to Table 5 it can be seen that, leathers tanned with sulphomethylated mimosa and quebracho tannins show higher hydrothermal stability values than leathers tanned with standard mimosa and quebracho. This quantitative increase is also significant statistically ($p=0.035$ for mimosa and 0.006 for quebracho samples). So the hydrothermal results are found acceptable comparing with the studies of John (1997), Dikmelik (1982) and Kite and Thomson (2006).

Basaran (1993) stated that, various physical tests have been developed to measure behaviour of this biological material under different effects and tensile strength, tear load and strength of grain tests have been also the most used ones among these tests.

Sharphouse (1995) advised that tensile strenght of skins tanned with vegetable tannins should be above 100daN/cm^2 . Ömür (2009) observed average tensile strenght and elongation at break values of vachetta leathers 31.30 N/mm^2 and 38.43% respectively. UNIDO has advised a minimum of 15N/mm^2 of tensile strenght for acceptable quality standards too. When tensile strenght values of leathers tanned with both modified and standard mimosa and quebracho are evaluated, it is seen that they match with quality standard limits. Additionally Freadiani et al (2008), found tensile strength values of 210.3 , 156.2 , 144.1 , 107.8 N/mm^2 for leathers tanned with various modified mimosa tannins.

No significant difference was found statistically for elongation at break values of leathers tanned with modified mimosa (M1) and quebracho (Q1) ($p=0,951$ and $p=0,710$). It is advised that elongation at break of vachetta for leather goods should be 70% maximum (TS 223, 1965). So the findings are compatible with the references.

As regards Table 5 is examined, it is seen that sulphomethylation modification causes a decrease in tear load values of leathers tanned with modified mimosa and an increase in the values of modified quebracho. This observed changes are also statistically significant ($p=0,036$ for mimosa and $p=0,003$ for quebracho). And again these tear load values are higher than the suggested figure of UNIDO guidelines for upholstery leathers which is a minimum of 40 N/mm. The tearing load values of modified leathers were also close to the values obtained at the studies of John (1997) and Özgünay (2005). Frediani et al (2008) found tear load values of 70.3, 63.4, 60.1, 45.9 N/mm for leathers tanned with various modified mimosa tannins.

Although strength and distension of grain by the ball burst test is an important test usually for shoe upper leathers, it is an important physical-mechanical test that obtains valuable information about the behaviour of grain for all types of leathers. Omur (2009) found average loads as 47.56 kgf and 62.68 kgf and distensions as 8.76 mm and 11.42 mm at grain crack and grain burst respectively for vachetta leathers. When we look at the Table 5, it is seen that strength of grain by the ball burst test decreases for Mimosa modification and increases for Quebracho modification yet these changes are not found to be statistically significant ($p=0.985$ and $p=0.822$).

Ecological and toxicological demands are playing an increasingly important role in the marketing of leather for all types of application. Manufacturers and consumers of leather goods have been paying much more attention to the residual monomer content of leather especially over the past two years. Formaldehyde initially came under scrutiny from automobile manufacturers, and shoe and garment manufacturers have followed in their footsteps (Wolf and Huffer, 2002). Because of that, in this research a necessity of determining the formaldehyde content of leathers tanned with modified tannins was considered. The formaldehyde content of leathers tanned with sulpho methylated mimosa was detected as 1.45 ppm and formaldehyde content of leathers tanned with sulpho methylated quebracho was detected as 2.28 ppm. OEKO-TEX (2015), has suggested

the limits of formaldehyde for leathers in direct contact with skin, leathers with no direct contact with skin, decoration material as 75 ppm, 300 ppm and 300 ppm respectively. The obtained results from the study were found below the limits.

CONCLUSIONS

- Leathers tanned with mimosa and quebracho show darkening and reddening with an increase in red and yellow tones when exposed to light for prolonged times. This is due to formation of phenyl radicals by the loss of hydrogen to atmospheric oxygen. These free radicals can lead to creation or linking of chromophore groups by polymerisation and results colouring.
- The random polymerisation of phenyl radicals can be oriented to a controlled modification of vegetable tannins with light stable synthetic tannin monomers. Mimosa and quebracho tannins can be modified by sulphitation, sulpho methylation and novalac synthesis.
- Although all the experimented modification types have more or less increasing effect on the lightfastness properties of mimosa and quebracho tanned leathers, sulpho methylation was found to be the most effective one.
- Leathers tanned with sulpho methylated mimosa and quebracho have clearly better stability to light than the ordinary mimosa and quebracho tanned leathers.
- When physical test results of leathers tanned with sulpho methylated mimosa and quebracho were compared to classic production, some changes in shrinkage temperature, tensile strength and tear load were statistically determined. However all the properties were found compatible with acceptable quality standards.
- As a final conclusion, sulpho methylation can be used in modification of mimosa and quebracho tannins to increase their stability to light; and the modified mimosa and quebracho tannins can be used in leather production without quality problems.

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