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

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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

INTRODUCTION

Vegetable tanning materials are preferred in production of sole leathers, shoe uppers, upholstery leathers and leather goods because of the favourable natural character they give to leathers but also they are more or less sensitive to light and they have the disadvantage of colour changing by exposure to light with time.

According to Pizzi *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 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 chromophore 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.

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

Material

10 pickled whole domestic hides each weighing approximately 10 kg, at pH 2.5, with their thickness adjusted to 1.4mm were used as the raw material for vegetable tanning. 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). 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.

Method

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

Sulphomethylation reaction occurs by the binding of sulphomethyl group ($-CH_2-SO_3R$), to the amine and amide compounds. This reaction has been widely used in urea and melamine based amino resin synthesis (Kasgoz, 1999).

In this modification 30% mimosa and quebracho tannins were modified with 8% sodium sulphide and 8% formaldehyde addition at 70 °C, based on pelt 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 were modified with 20% phenol sulfonic acid, 1.5% urea and 5.5% formaldehyde based at 75 °C, based on pelt weight. Then the modification was completed by addition of 12.5% sodium sulphide.

Sulphitation

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.

In this modification 30% mimosa and quebracho tannins were modified with 12.5% Sodium sulphide based on tannin weight at 70 °C. Then the modification was completed by addition of 5% UVS-HALS.

Tanning Process

Before vegetable tannage the pH value of pickled pelts were adjusted to pH 5.5 by depickling process. The hides were tanned by using the vegetable tanning process illustrated in Table 1. Then the leathers were dried in a dark place and mechanical processes like milling and toggling were carried out.

Table 1. 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

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 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: 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).

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 2 and Table 3 in CIE Lab coordinates.

Table 2. Colour Change Measurements of Leathers Tanned with Non-Modified and Modified Mimosa Tannins

	Before			After			
Leather Sample	L	a	b	L	a	b	dE
M0	69.42	8.28	12.21	55.85	17.18	29.51	23.72
M1	46.24	12.25	18.35	42.47	17.94	25.28	9.72
M2	64.28	12.74	19.51	46.59	20.46	29.90	21.91
M3	50.94	10.39	14.56	53.43	13.19	28.45	14.38

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

	Before			After			
Leather Sample	L	a	b	L	a	b	dE
K0	67.07	12.20	20.59	51.61	18.63	28.99	18.73
K1	45.77	13.53	19.8	43.1	20.7	27.93	11.16
K2	44.03	17.37	23.34	30.06	16.97	12.75	17.54
K3	63.63	12.30	21.71	51.84	19.27	29.76	15.89

According to the results in Table 2 and Table 3, the lowest colour changes are observed from the leathers which were tanned with sulphomethylated mimosa and quebracho tannins (M1 and K1). 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 4.

Table 4. Physical Test Results of Leathers Tanned with Standard and Modified Mimosa and Quebracho Tannins

Leather Sample	Ts (ºC)	Tensile strength (N/mm^2)	Elongation (%)	Tear load (N/mm)	Strength of grain (kgf)
M0	83,77	29,86	30,01	85,55	100
M1	92,23	19,87	31,46	65,78	96,5
K0	79,45	21,83	27,66	58,48	92,5
K1	83,85	20,24	31,48	78,15	100

According to Table 4 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.

UNIDO has advised a minimum of $15N/mm^2$ of tensile strength for acceptable quality standards. When tensile strength values of leathers tanned with both modified and standard mimosa and quebracho are evaluated, it is seen that they match with quality standard limits.

No significant difference was found for elongation at break values of leathers tanned with modified mimosa (M1) and quebracho (Q1). 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 4 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. 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 Ozgunay (2005).

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. When we look at the Table 4, 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.

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.

REFERENCES

Covington, A.G. (2009), *Tanning Chemistry*, Royal Society of Chemistry Publishing, Northampton.

Frediani, P., Tambi, L. and Frediani M. (2008), “Hide Tanning with Modified Natural Tannins”, *Journal of Applied Polymer Science*, 108,1797–1809.

John, G. (1997), *Possible Defects in Leather Production*, Druck Partner Rübelman GmbH, Hemsbach.

Kaşgöz, H. (1999), “Modifiye Poliakrilamidler ve Uygulamaları”, İstanbul Üniversitesi Fen Bilimleri Enstitüsü, Doktora Tezi, İstanbul.

OEKO-TEX (2015), https://www.oekotex.com/en/manufacturers/test_criteria/ limit_values/limit_values.html, (Visited May 3rd, 2015).

Omur, S., Mutlu, M.M. (2016), “Modification Of Mimosa And Quebracho Tannins and the Lightfastness Properties of the Proccessed Leathers”, *Tekstil ve Konfeksiyon*, 26(2), 230-235.

Ozgunay, H. (2000), “Meşe Palamutu Ekstarktı Valeksin Deri Sanayiinde Kullanılabilirliğinin Artırılması Üzerine Araştırmalar”, Ege Üniversitesi Fen Bilimleri Enstitüsü Yüksek Lisans Tezi, İzmir.

Ozgunay, H. (2008), “Light Fastness Properties of Leathers Tanned with Various Vegetable Tannins”, *Journal of the American Leather Chemists Associations*, 103, 345-351.

Pizzi, A., Simon, C., George, B. and Triboulot, M.C. (2004), “Leather Light Stability/Tannins Antioxidant Characteristics for Leather Made with Vegetable Tannins/MUF Resins”, *Journal of the American Leather Chemists Associations*, 99, 1-11.

TS 223 (1965), Vaketa Mamul Deri, Türk Standartları Enstitüsü, Ankara.

TS 4117 EN ISO 2589 (2006), Kalınlık Tayini Türk Standartları Enstitüsü, Ankara.

TS 4120 EN ISO 3380 (2005), Determination of shrinkage temperature, Türk Standartları Enstitüsü, Ankara.

TS 4131 (1985), Sırça Dayanımı ve Gerilebilirlik Tayini- Bilye Patlama Deneyi, Türk Standartları Enstitüsü, Ankara.

TS EN ISO 105-B02 (2014), Yapay ışığa karşı renk haslığının tayini- Ksenon ark soldurma lambası deneyi, Türk Standartları Enstitüsü, Ankara.

TS EN ISO 17226-1 (2009), Fomaldehit İçeriğinin Kimyasal Tayini-Bölüm 1: Yüksek Performans Sıvı Kromotografik Yöntem, Türk Standartları Enstitüsü, Ankara.

TS EN ISO 2418 (2006), Kimyasal, Fiziksel, Mekanik Renk Haslığı Deneyi Numune Alma Bölgesi, Türk Standartları Enstitüsü, Ankara.

TS EN ISO 2419 (2012), Numune hazırlama ve şartlandırma, Türk Standartları Enstitüsü, Ankara.

TS EN ISO 3376 (2012), Çekme Mukavemeti Ve Uzama Yüzdesinin Tayini, Türk Standartları Enstitüsü, Ankara.

TS EN ISO 3377-1 (2012), Yırtılma Yükü Tayini, Bölüm 1: Tek Kenar Yırtığı, Türk Standartları Enstitüsü, Ankara.

UNIDO (1994), *Acceptable Quality Levels in Leathers*, United Nations Publications, New York.

UPAC (1997), *Compendium of Chemical Terminology*, Blackwell Scientific Publications, 2nd ed., Oxford.

Wolf, G. and Hüffer, S. (2002), “Formaldehyde in Leather-A Survey”, *Journal of the American Leather Chemists Associations*, 97, 456-464.