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DETERMINING LIGHTFASTNESS PROPERTIES OF VEGETABLE TANNINS AND CHEMICAL PROPERTIES OF THE LEATHERS TANNED WITH MODIFIED MIMOSA AND QUEBRACHO

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Abstract: *The vegetable tannins are the oldest tanning agents used in leather industry. They give their natural character and colour to the leathers which they are applied to, but they have the disadvantage of colour change when they are exposed to light for prolonged times. In this study light fastness properties of leathers tanned with mimosa, quebracho, valonea and chestnut tannins were measured. Lightfastness properties of mimosa and quebracho tannins were found lower. Then these tannins were modified with sulphitation, novalac synthesis and sulphomethylation processes. Lightfastness and determination of volatile matter, determination of matter soluble in dichloromethane, determination of sulphated total ash and sulphated water-insoluble ash, determination of water soluble matter, water soluble inorganic matter and water soluble organic matter, determination of nitrogen content and hide substance, calculation of degree of tannage determination of formaldehyde content analyses were performed to the leathers tanned with modified mimosa and quebracho tannins. From comparison of results, it was understood that sulpmethylation process can be used for production of leathers with higher lightfastness and without major change on chemical properties. When chemical properties of leathers tanned with modified quebracho and mimosa are considered: volatile matter, sulphated total ash and sulphated water- insoluble ash, water soluble matter, water soluble inorganic matter and water soluble organic matter, hide substance and formaldehyde contents were found compatible with standard mimosa and quebracho. However degree of tannage and matter soluble in dichloromethane values were found lower, which means some enhancements in modification or fatliquoring process should be considered.*

Key words: *Leather, Lightfastness, Vegetable Tannins*

1. INTRODUCTION

The leather-tanning industry is one of the most ancient in operation. Although the technology of leather manufacture has evolved over centuries, the basic principles for the production of leather have remained the same. Hide proteins, mainly collagen, are rendered insoluble and dimensionally more stable by treatment with chemical products able to fix on them and render them both more resistant to mechanical wear and less susceptible to biological and other types of attack. Forestry-derived, natural polyphenolic tannins and polyflavonoid extracts, used mainly for the manufacture of heavy, rigid, and hard leathers for shoe soles, saddles, belts, and other implements subject to high wear, are one of the main products still used today for leather tanning. Natural polyphenolic tannins have a strong astringent effect and give considerable hardness, and toughness to the leather produced with them. They present, however, among others, the considerable disadvantage to have marked darkening problems when exposed to light. [1].

The vegetable tannins are obtained from wood, bark, fruit, seed and leaves of some trees. Mimosa and quebracho tannins are obtained from wood part of trees and chemically they belong to the condensed group of tannins. Chestnut and valonea tannins are obtained from wood and fruit part of the trees and belong to the hydrolysable group of vegetable tannins. The tannins behave like dyestuffs and the hides also get the colour of the tannin itself. Especially the hides tanned with mimosa and quebracho becomes brownish colours. The valonea and chestnut tannins give leather pale colours of yellow.

While the condensed tannins have a flavonoid structure and contains benzene rings they are sensitive to light, especially to the UV light which have highest energy level in sunlight. 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. [2].

The variation of leather colour as a function of aging 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 reaction due to the photo degradation of the system [1]. Light fastness of dyed textiles is related to the chemical structure and physical characteristics of the fibre itself [3].

In this research firstly, the colour changing of mimosa, quebracho, chestnut and valonea tanned leathers which were exposed to light according to lightfastness test conditions, had been measured. After definition of which tannin group had the most colour change, some modification processes, like sulphomethylation, sulphitation and novalac synthesis were applied. Then, all the hides were tanned with these modified tannins, and colour measurement tests and chemical analyses were performed to these leathers. The aim of the study was to test and enhance lightfastness properties of vegetable tannins without major quality change in final leathers.

2. EXPERIMENTAL

2.1. Material

10 pickled domestic hides each weighting approximately 10 kg and at pH 2.5 were used as the raw material for vegetable tanning. The thicknesses of pickled hides were adjusted to 1.4 mm.

Commercial mimosa, quebracho, chestnut and valonea tannins were used for tanning. Modified quebracho and mimosa were obtained by sulphomethylation, novalac synthesis and sulphitation processes [4].

2.2. Method

2.1.1. Tanning Process

Before the main vegetable tannage, a depickle process was applied and pH of pickled leathers were adjusted to pH 5.5 Then, the leathers 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.

2.1.2. Lightfastness tests and Colour Measurement

For the evaluation of stability of vegetable tanned leathers to the light, the light fastness test was carried out according to ISO 105-B02 [5], after that determination of colour change in leather surfaces were detected by the colour change tests according to ISO 105-A05 [6].

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

2.1.3. Chemical analysis of tanned leathers

The analyses were carried out using TSE ISO standards. The tests were performed on samples of leather collected and treated as reported in methodology [7], [8]. Determination of volatile matter [9], matter soluble in dichloromethane [10], sulphated total ash and sulphated water-insoluble ash [11], water soluble matter, water soluble inorganic and organic matter [12], nitrogen content and hide substance [13] and calculation of degree of tannage [14] were performed. Chemical determination of formaldehyde content was performed according to the standard [15].

3. RESULTS AND DISCUSSION

Colour measurements of leathers tanned with mimosa, quebracho, valonea and chestnut before and after the light fastness tests are given in Table 2. “0” indicates not exposed to test light and “1” indicates exposed to test light. dE figure shows the colour difference which means the lower value it is, the less colour change occurs.

Table 2: *Colour Measurements of Leathers before and after Lightfastness Tests*

Tannin Type	**L**	**a**	**b**	**dE**
Mimosa 0	44.87	14.57	17.46	
Mimosa 1	29.29	20.01	16.12	16.55
Quebracho 0	52.39	18.24	25.40	
Quebracho 1	31.51	21.64	17.92	22.44
Valonea 0	44.55	7.26	19.36	
Valonea 1	40.29	9.91	21.38	5.40
Chestnut 0	53.50	8.15	21.66	
Chestnut 1	46.54	10.14	25.54	8.21

From Table 2, it is seen that colour changes of leathers tanned with condensed tannin tanned were found higher than the hydrolysable ones. So it can be understood that, the condensed tannins are more sensitive to exposure to light and so their colour can change more. Ozgunay (2008) has stated that condensed tannins change their color more and more rapidly than hydrolysable tannins due to their polyflanoid structures. [16].

Due to the reason that light fastness properties of quebracho and mimosa tanned leathers were lower than the others, these tannins were chosen for modification processes. Non-modified quebracho, sulphomethylated quebracho, novalac synthesis quebracho and sulphited quebracho were coded as KS, K1, K2 and K3 respectively. Non-modified mimosa, sulphomethylated mimosa, novalac synthesis mimosa and sulphited mimosa were coded as MS, M1, M2 and M3 respectively.

Colour measurements of the leathers tanned with non-modified and modified mimosa and quebracho are shown in Table 3.

Table 3: *Lightfastness test results of modified quebracho and mimosa tannins*

Sample Code	L	a	b	dE
KS	51.61	18.63	28.99	18.73
K1	43.1	20.7	27.93	11.16
K2	30.06	16.97	12.75	17.54
K3	51.84	19.27	29.76	15.89
MS	55.85	17.18	29.51	23.72
M1	42.47	17.94	25.28	9.72
M2	46.59	20.46	29.90	21.91
M3	53.43	13.19	28.45	14.38

As it can be seen in Table 3, the dE value which is the criteria of colour change of leather was obtained the lowest from the sulphomethylation modification of quebracho and mimosa tannins.

Since the modification of tannins differs the lightfastness properties, it can also affect the chemical properties of leathers. So the chemical properties of non-modified and modified quebracho and mimosa tanned leathers were measured and the results are shown in Table 4.

Table 4: *Chemical Analysis on Leather Tanned with Modified Quebracho and Mimosa Tannins*

Leather Sample	**Volatile matter**	**Matter soluble in dichloromethane**	**Sulphated total ash**	**Water soluble matter**	**Hide Substance**	**Degree of Tannage**	**Formaldehyde Content**
KS	7.09	4.00	0.31	0.72	56.91	54.37	0.95
K1	7.62	2.93	0.76	0.71	61.82	42.30	2.28
K2	7.87	2.70	0.47	0.52	69.19	28.54	1.46
K3	7.12	4.11	0.32	0.71	61.82	41.48	1.09
MS	6.95	3.39	0.17	0.67	59.35	49.67	0.87
M1	8.37	1.06	0.68	0.60	69.30	29.05	1.45
M2	7.93	2.63	0.19	0.37	61.86	43.65	1.23
M3	7.11	3.28	0.58	0.75	69.30	24.43	1.66

Determination of volatile matter in leather is affected from climatic conditions, tanning type, fatliquoring and unfixed organic and mineral materials. The dryness of leather causes crinkle grain and loss in leather surface. Higher rates can result looseness in leather structure [17]. Ozgunay (2000) found volatile matter 7.05 % for non-modified valonea tannin and 6.2 % for thiosulphate modified one [18]. As seen from Table 4, values for volatile matter of leathers are similar.

In leather production procedure some fatliquoring agents have been used for providing softness and flexibility of leather fibres. UNIDO (1994) suggests that matter soluble in dichloromethane value should be in a range of 3-12 % [19]. In this research these values were found lower from the values suggested in the literature for the leather samples of K1, K2, M1 and M2; although same production recipe and same amount of fatliquor were used. However this can be adjusted by using different or more fatliquoring .

In beamhouse operations some organic and inorganic chemicals are used for transformation of raw hide to the leather. It is required to keep the inorganic matter amount as low as possible. If the sulphated total ash value is higher, it shows that there are much inorganic matters left or used. So this affects the leather quality too [18]. In literature [17], this value advised no to be not higher than 2.5 % for vegetable tanned leathers. The values for this research seem suitable for advised limits.

It is mentioned that water soluble matter value should not be higher than 6% for vegetable tanned leathers[20]. As seen in Table 6, the these values are lower and compatible with the literature.

Ozgunay (2000) found that, modification of valonea with sodium meta bisulphide gives the hide substance content of 45.90% for vegetable tanned leathers [18]. As shown in Table 4 the hide substance content of leathers tanned with modified and non-modified tannins are higher than 45 %.

Degree of tanning indicates the amount of vegetable tannin fixed to 100g of skin substance. It should be at least 50 for vegetable tanned leather; values below 50 indicate that penetration of tannin might be inadequate [17]. From the Table 4, it is clear that the degree of tannage values for non-modified mimosa and quebracho tannins are exactly 50 or upper degree. But the value for the leathers tanned with modified tannins is below from the value of 50. So it may be because of the higher molecular structure of modified tanning agents causing inadequate penetration to the hides.

Ecological and toxicological demands are playing increasingly important role in the marketing of leather. Formaldehyde initially came under scrutiny from automobile manufacturers, and shoe and garment manufacturers have followed in their footsteps [21]. In literature [22], it has been suggested the limits of formaldehyde for leathers in direct contact with skin, leathers with no direct contact with skin, decoration material as 75ppm, 300ppm and 300ppm respectively. From the Table 4 it appears that the obtained results from the study are found below the limits.

4. CONCLUSIONS

In leather technology, vegetable tannins are widely used tanning agents which can give their own colour to the leather while tanning process. However these colours are not stable to light most of the time and this can cause quality problems in consumer leather goods. The lightfastness is a very important property for all type of leather goods. The sun light or mainly strong light may affect the colour of the leather surface. Most of coloured organic surfaces, e.g. leather, textile, and wood have the disadvantage of discolouring, namely fading or reddening.

In this research it has been found that the condensed tannins; mimosa and quebracho, are more sensitive to exposure to the light. They quickly turn the leather surface to reddish colour, called reddening. So some modification processes were applied to them to enhance their lightfastness properties. Accordingly sulphomethylation, novalac synthesis and sulphitation trials were applied and modified tannins were obtained. The lightfastness properties of the leathers tanned with sulphomethylated mimosa and quebracho were found better than non-modified ones and then the other modifications. So this modification was found successful in terms of lightfastness. Afterwards chemical tests have been applied to the leather samples to determine if these modifications had any effect on chemical properties of leathers. When chemical properties of leathers tanned with modified quebracho and mimosa are considered: volatile matter, sulphated total ash and sulphated water-insoluble ash, water soluble matter, water soluble inorganic matter and water soluble organic matter, hide substance and formaldehyde contents were found compatible with standard mimosa and quebracho. However degree of tannage and matter soluble in dichloromethane values were found lower, which means some enhancements in modification or fatliquoring process should be considered.

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