African Journal of Biotechnology Vol. 7 (20), pp. 3737-3742, 20 October, 2008
Available online at http://www.academicjournals.org/AJB
ISSN 1684–5315 © 2008 Academic Journals

Full Length Research Paper

An investigation about the effect of oxazolidine on modified valonia extract tanning

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Accepted 9 September, 2008

This study is aimed at combining the usage of valonia and modified valonia extracts with oxazolidine to obtain an increase in hydrothermal stability, and thus to develop tanning efficiency and to produce leathers that have better properties then the ones tanned with valonia extract only. Natural and three modified valonia extracts and oxazolidine were used as tanning materials. Skin samples were divided into two groups. In group A, valonia extracts were used as tanning materials and oxazolidine as retanning agent. Group A was divided into 4 subgroups according to the used extract type. Each subgroup was also separated into four lots according to the oxazolidine percentages used. Group B; where oxazolidine was used as pretanning while valonia extracts as tanning agents, was divided into three subgroups according of oxazolidine usage. Each subgroup had four lots according to the used extracts. General means of Shrinkage Temperatures (Ts) for natural extract, group A and B were found as 65.66, 78.62 and 83.42°C, respectively, indicating that the oxazolidine pretanning followed by valonia retanning provides better tanning efficiency. On the base of the unique experiment, 4% oxazolidine and 20% least modified vegetable tannin combination gave the best result.

Key words: Leather, tanning, tannin, valonia, oxazolidine, vegetable, shrinkage temperature.

INTRODUCTION

Vegetable tannins and tanning have kept their importance for thousands of years. Up till present, many researches on vegetable tannins have been conducted on both single and combined use with other vegetable tannins, aldehydes, syntans and various metal salts. Although the vegetable tannins are thought as alternatives of chromium salts, characteristics of the leather properties and tanning systems have remained second to chrome and have not yet reached perfection; but new attempts are being made continuously (Madhan, 2006). On the other hand, oak trees, which produce tannin of valonia, grow in western parts of Turkey and its extract is known as valex. This research was aimed to combine the usage of valonia and modified valonia extracts together with oxazolidine to obtain an increase in hydrothermal stability, and thus to have better tanning efficiency and to produce leathers that have better properties than single valonia tanned ones. Furthermore, an increase in the demand of valonia extract can also be expected.

On the other hand, chrome is still a problem for the leather industry. For example, chrome (III) turns into chrome (VI) in both waste and leather with the effect of various factors. Discharge of chrome containing wastes have been restricted by environmentalists and laws due to chrome (VI) which has allergenic, toxic, mutogenic and also carcinogenic properties. Because of these handicaps, many researches have been carried out with the intent to find alternatives to chrome tanning by making use of new tanning materials and methods (Afsar and Basaran, 2001). Vegetable tanning has always been one of the most important alternatives as an environment friendly system and for that reason, researches on vegetable tannin combinations with oxazolidines, syntans, metal salts and others have been focused on (Ya-Ting, 2007; Shi et al., 2000).

Vegetable tannins with high molecular weights include lots of pheonolic OH groups and complicated organic materials. They are colloidal and soluble in alcohol, alcohol ether mixture and partly in acetic acid. They are not soluble in waterless ether, petroleum ether and chloroform. But they can easily change their structures through

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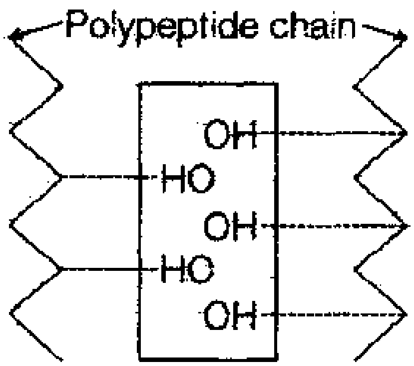
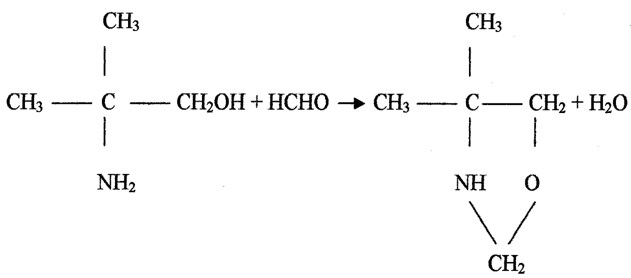


Figure 1. Cross-linkage of vegetable tannins with polypeptide chain.



Oksazolidin (I) A : 4,4-Dymethyl-1,3-oxazolidine

Figure 2. Oksazolidin (I) A: 4,4-dymethyl-1,3-oxazolidine.

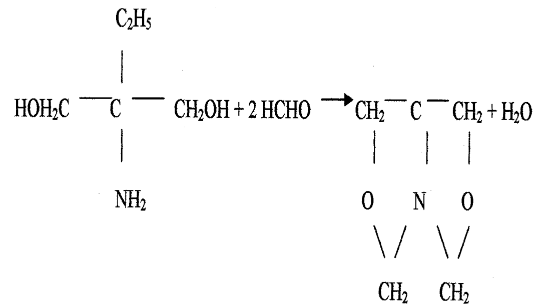


Figure 3. Oksazolidin (II) E: 1-azo-3,7-dioxabcyclo-5-ethyl-(3,3,0)-octane.

oxidative, reductive and enzymatic effects. When they are heated, they do not dissolve but carbonize. They generate sediment with gelatine, adhesive solutions, alcoholoids, amines and metal salts. Also they give characteristic colour reactions with iron salts. Vegetable tannins are astringent and hygroscopic. With increasing temperatures, their viscosity rise. They are polyphenolic compounds, able to associate and combine with protein mainly by hydrogen bonds (Bickley, 1992).

Vegetable tannins are classified into two groups as hydrolysable tannins (pyrogallol) and condensed tannins (pyrocatechin). Hydrolysable tannins are liable to decomposition by hydrolysis. They include gallotannins, derivatives of gallic acid and ellagitannins and derivatives of ellagic acid. Their phenolic aromatic compounds with oxygen atom combined with glucose molecule by ester bonds. Hydrolysable tannins are categorized in three sub-groups as depsides, gallotannins and ellagitannins. Myrobalan, chestnut, valonia, sumac, tara and divi divi are examples of hydrolysable tannins (Slabbert, 1999).

Condensed tannins are not decomposed by hydrolysis but liable to oxidation and polymerisation to form insoluble products. Their principal molecules are flavan-3-ol and flavan-3,4-diol. Condensed tannins have more stable composition than hydrolysable tannins, which cause phenolic aromatic compounds to combine with carbon atoms. Mimosa, quebracho, hemlock, willow and gambir are few examples of condensed tannins (Teliba et al., 1993).

Cross-linkage is affected by phenolic OH groups of vegetable tannins with carbonamid groups of collagen through hydrogen bridges. In other words, the cross-linking between leather and vegetable tannins are based on hydrogen bridges. Hydrogen atoms of OH groups react with oxygen atoms of peptide groups in collagen (Figure 1). The hydrogen bridges are optimal in acidic environment (BASF, 2006; Covington, 2001; Haslam, 1966).

The other main chemical compound, which was used in the research, was oxazolidine. Oxazolidines are heterocyclic derivatives prepared from various amino alcohols and formaldehyde. Although they possess some of the properties of aldehydes, oxazolidines, which are multifunctional agents, do crosslink with phenols and proteins. They can be used as pretanning or retanning agents. Tanning with oxazolidines increases the shrinkage temperature of the leather (Ts). Oxazolidines are industrially important due to their ability to react with Novalac phenolic resins. These are large molecules obtained from condensation of phenols and cresols with formaldehyde. They also react with resorcinol, epoxies and proteins (Prentiss et al., 2003).

The three most commonly encountered oxazolidines are oxazolidine I(A), II(E) and T. Oxazolidine A and E are yellowish liquids. T is an off-white solid. The chemical formulations of the three products are shown in Figures 2, 3 and 4.

Oxazolidine I reacts too rapidly with protein and are applied as pretanning agent, to increase the shrinkage, temperature of pickled pelts for aqueous degreasing at higher temperatures, thus leading to more efficient degreasing. Although no theory has been offered for the reaction of oxazolidines with hide protein, a reasonable explanation seems to be that cross-linkage may occur through the opening up of the heterocyclic rings by hydrolysis, followed by cross-linkage with amino groups in the protein chain (Gill, 1985; Shi et al., 1999).

Oxazolidine II gives good results with chrome and vegetable tanning agents. The shrinkage temperatures (Ts)

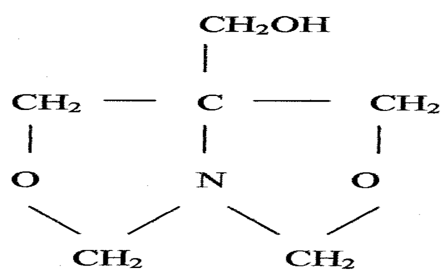


Figure 4. Oksazolidin T: Hydroxymethyl-1-azo-3,7-dioxabcyclo-(3,3,0)-octane.

of leathers produced by combination tannages of condensed tannins + oxazolidine II (E) and hydrolysable tannins + oxazolidine II (E) are quite different. When 20% condensed tannin based on pickled pelt weight was used, Ts of leathers easily reached up to 100℃ after retannage with 4 - 6% oxazolidine II (E). On the other hand, when hydrolysable tannins were used, the increase of Ts after retanning with oxazolidine II (E) was only a few degrees. It is suitable to be used in all types of leathers; especially in the tanning of wool-on leathers, it gives positive results on wool colour. Oxazolidine T has not proved as useful as others yet (Shi et al., 2001).

MATERIALS AND METHODS

Materials

Experiments were conducted with 94 halves of pickled kidskins that have same uniform properties (Beck and Rowlands, 1970). Natural and three modified valonia extracts and oxazolidine were used as tanning materials. Commercial grade of chemicals were used in processing of the skins. Oxazolidine II, as Edaplin VA *ex.* (Munzig Chemie) was used in an activity of 100% and sodium hydrogen sulphite (Merck) was at analytical reagent grade. Valonia extract (67% tannin) was supplied by the Balaban Company in Turkey.

Methods

The valonia extracts were modified. To achieve this, the extracts (based on the pickled weight) were dissolved by warm distilled water and heated up to 65 ± 2°C. For the three types of modifications, sodium hydrogen sulphides were prepared as 5, 10 and 15% of valonia weights and added to each valonia solution drop by drop at fixed temperature and the reactions were carried on for one more hour. Therefore, Modified Valonea Extracts of I, II and III were prepared in accordance with the different sulphites concentrations.

According to the experimental design, skin samples were divided into two main groups according to the tanning systems. Three skins were used in each experiment. In the first group called A, valonia extracts were used as tanning materials in a fixed ratio of 20% and oxazolidines as retanning agent. Group A was divided into 4 subgroups according to the used extracts types. And all subgroups were also separated into four lots according to the used oxozolidine percentages (0, 2, 4 and 6%) as retanning materials.

In group B, oxazolidines were used as pretanning materials and extracts as tanning agents. It had also three subgroups (2, 4, 6%) of oxazolidine. Each subgroup had four lots according to the used extracts, 1.e. natural and three modified ones. The distributions of groups A and B are given in Tables 1 and 2.

After processing (Tables 3 and 4), thermal stabilities of the leathers showing tanning efficiency were determined. In the tests of the leathers, related methods of the International Union of Leather

Table 1. Distrubution of subgroubs in Group A.

NV : Natural Valonia Extract	**A_1**
MV_I : Modified Valonia Extract I	**A_2**
MV_{II}: Modified Valonia Extract II	**A_3**
MV_{III} : Modified Valonia Extract III	**A_4**
0% Oxazolidine	**a_1**
2% Oxazolidine	**a_2**
4% Oxazolidine	**a_3**
6% Oxazolidine	**a_4**
Vegetable Tanning and Oxazolidine Retanning:	
A_1 a_1	20% NV + 0% Oxazolidine
A_1 a_2	20% NV + 2% Oxazolidine
A_1 a_3	20% NV + 4% Oxazolidine
A_1 a_4	20% NV + 6% Oxazolidine
A_3 a_1	20% MV_{II} + 0% Oxazolidine
A_3 a_2	20% MV_{II} + 2% Oxazolidine
A_3 a_3	20% MV_{II} + 4% Oxazolidine
A_3 a_4	20% MV_{II} + 6% Oxazolidine
A_4 a_1	20 %MV_{III}+ 0% Oxazolidine
A_4 a_2	20% MV_{III}+ 2% Oxazolidine
A_4 a_3	20% MV_{III}+ 4% Oxazolidine
A_4 a_4	20% MV_{III}+ 6% Oxazolidine

Table 2. Distrubution of subgroubs in Group B.

2% Oxazolidine	**B_1**
4% Oxazolidine	**B_2**
6% Oxazolidine	**B_3**
NV : Natural Valonia Extract	**b_1**
MV_I: Modified Valonia Extract I	**b_2**
MV_{II}: Modified Valonia Extract II	**b_3**
MV_{III} : Modified Valonia Extract III	**b_4**
Oxazolidine Pretanning and Vegetable Tanning	
B_1 b_1	2% Oxazolidine + 20% NV
B_1 b_2	2% Oxazolidine + 20% MV_I
B_1 b_3	2% Oxazolidine + 20% MV_{II}
B_1 b_4	2% Oxazolidine + 20% MV_{III}
B_2 b_1	4% Oxazolidine + 20% NV
B_2 b_2	4% Oxazolidine + 20% MV_I
B_2 b_3	4% Oxazolidine + 20% MV_{II}
B_2 b_4	4% Oxazolidine + 20% MV_{III}
B_3 b_1	6% Oxazolidine + 20% NV
B_3 b_2	6% Oxazolidine + 20% MV_I
B_3 b_3	6% Oxazolidine + 20% MV_{II}
B_3 b_4	6% Oxazolidine + 20% MV_{III}

Table 3. Process recipe of Group A.

Process	Product	Amount (%)	Temperature (°C)	Duration (min)	Notes
Depickle	Water	150	20-25	10	10 °Bé
	Sodium formate	1		40	pH : 4.0
	Sodium bicarbonate	1.5		40	pH : 6.6; drain
Tanning	Water	100	20		
	Valonia	10		90	
	Valonia	10		120	Over night in the float
					Morning 60 min run
	Water		20	90	
	Formic acid	0.25		90	
Retanning	Water	200	20		Horse up
	Oxazolidine	X	35	60	
			40	60	
			50	60	
			60	60	
					Horse up

Weight: Pickled Weight + 50%.

Table 4. Process recipe of Group B.

Process	Product	Amount (%)	Temperature (°C)	Duration (min)	Notes
Depickle	Water	150	20-25	10	10 °Bé
	Sodiumformate	1		40	pH : 4.0
	Sodium bicarbonate	1.5		40	pH : 6.6; drain
Pre-Tanning	Water	200	20		
	Oxazolidine	X	35	60	
			40	60	
			50	60	
			60	60	
					Horse up
Retanning	Water	100	20		
	Valonia	10		60	
	Valonia	10		120	
			35	60	
			40	60	
			50	60	
			60	60	
					Horse up

Weight: Pickled Weight + 50%.

Technologists and Chemists Societies (IULTCS) official methods of analysis for leather such as: IUP 2 “Sampling”; IUP1&3 “Conditioning”; IUP 4 “Measurement of thickness” and IUP 16 “Measurement of shrinkage temperature up to 100°C” were used (IULTCS, 2008).

RESULTS AND DISCUSSION

Natural extract application gave a 65.66°C of mean shrinkage temperature (Ts). General mean of shrinkage temperature for group A was found as 75.38°C. Means of subgroups A_1, A_2, A_3, and A_4 were 76.08; 75.50; 75.75; and 74.20°C, respectively. All results related to group A are given in Table 5.

Group B in which primarly oxazolidines were used as pretanning agents had a general mean of shrinkage temperature value as 83.42°C. Means of subgroups B_1, B_2 and B_3 were also found as 83.96; 84.76 and 81.53°C, respectively. The results related to group B are shown in Table 6.

When the results of group A were taken into considera-

Table 5. Findings related shrinkage temperature (Ts) for Group A.

20% Valonia	% Oxazolidine	T_s Min	T_s Max	T_s X±Sx
NV	0	65	67	65.66±1.15
	2	77	81	79.00±2.00
	4	79	82	79.66±2.08
	6	79	81	80.00±1.00
Mean				76.08±6.44
MV_I	0	65	67	65.66±1.15
	2	76	79	77.33±1.52
	4	77	79	78.00±1.00
	6	81	81	81.00± 0,00
Mean				75.50±6.17
MV_{II}	0	65	67	65.66±1.15
	2	76	78	77.00±1.00
	4	79	80	79.33±0.57
	6	80	82	81.00±1.00
Mean				75.75±6.31
MV_{III}	0	65	67	65.66±1.15
	2	72	73	72.33±0.57
	4	78.5	79	78.83±0.28
	6	79	81	80.00±1.00
Mean				74.20±6.02
General Mean		74.20	76.08	75.38±6.08

Table 6. Findings related shrinkage temperature (Ts) for Group B.

% Oxazolidine	% Valonia	T_s Min	T_s Max	T_s X±Sx
2	20 NV	84	86	85.33±1.15
2	20 MV_I	82.5	83.5	83.00±050
2	20 MV_{II}	81	81.5	81.16±0.28
2	20 MV_{III}	80	81.5	80.33±0.76
Mean				83.96±3.36
4	20 NV	84	85	84.66±0.57
4	20 MV_I	85	85	85.00±0.00
4	20 MV_{II}	83.5	85	84.16±0.76
4	20 MV_{III}	81	81.5	81.16±0.28
Mean				84.76±2.56
6	20 NV	80	81	80.33±0.57
6	20 MV_I	80	81	80.66±0.57
6	20 MV_{II}	80	81	80.33±0.57
6	20 MV_{III}	79	81	80.00±1.00
Mean				81.53±2.56
General Mean		81.53	84.76	83.42±3.11

ration, it was clearly determined that shrinkage temperatures increased along with increasing amount of oxazolidine. Subgroup of $A_1a_{1...}a_4$ had a minimum of 65.66°C and maximum 80.00°C of shrinkage temperatures with a mean of 76.08°C. As for A_2 $a_{1...}a_4$; minimum, maximum and mean were 65.66; 81.00 and 75.50°C, respectively. The subgroup of $A_3a_{1...}a_4$ had the same parameters as minimum and maximum but mean was 75.75°C. In the last subgroup named A_4 $a_{1...}a_4$, the three mentioned values were 65.66, 80.00 and 74.20°C in the given order. The general mean was 75.38°C.

When the group B was evaluated, $B_1b_{1...}b_4$ minimum, maximum and mean were 80.33, 85.33 and 83.96°C, respectively. Subgroup of $B_2b_{1...}b_4$ had a minimum of

81.16°C and maximum of 85.00°C with a mean 84.76°C. In the last subgroub of $B_3b_{1...}b_4$, the three values were 80.00; 80.66 and 81.53°C, respectively. The general mean was 83.42°C.

Covington and Shi (1998) declared that especially for the condensed tannins, tanning with vegetables and retanning with oxazolidine gives better shrinkage temperature values. For example, 20% mimosa in combination with 2, 4 and 6% oxazolidine gave 108, 114 and114°C shrinkage temperature values, respectively. Valonia and chestnut gave lower values of 88, 88 and 87, and 86, 85 and 84°C, respectively. In adverse application, mimosa and chestnut gave 96, 97 and 100, and 81, 81 and 83°C shrinkage temperatures, respectively. The data about chestnut which belong to ellagitannin subgroup of hydrolysable tannins were alike to our findings because of its similar chemical structure with valonia as mentioned by Ozgunay et al. (2007). There is no data on valonia to compare with our findings for that kind of application.

Shi et al. (2001) had also continued their research with natural valonia and oxidised valonia extracts along with chrome and aluminium combinations. 15% valonia extract gave 74°C Ts whereas 5, 7 and 10% oxidised extracts gave 59, 62 and 66°C Ts, respectively. These shrinkage temperature values can be enhanced in combination with mineral tanning agents up to 100°C.

According to our study, modified extracts and oxazolidines gave better results than only natural extract application. General mean of shrinkage temperature for group B (83.42°C) was found superior than group A (75.38°C) and that means oxazolidine pretanning followed by valonia tanning had better tanning efficiency. On the base of the unique experiment, 4% oxazolidine and 20% least modified vegetable tannin combination gave the best result among others.

ACKNOWLEDGMENT

The authors wish to thank Ege University Research Fund Accounting Office for financial support under Project MUH 006.

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