

SUMAC APPLICATION FOR VEGETABLE TANNING IMPROVEMENT

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In our research the advantages and disadvantages of sumac, as vegetable tanning agent were analyzed. Tanning using sumac tannides and aluminum compounds after hide pretreatment by phosphonium compounds for increase of leather aging resistance was developed. Obtained leather has shrinkage temperature from 90 to 95°C and good physical-chemical characteristics. IR-spectroscopy was employed to investigate the nature of interaction between the sumac and collagen. As a model of collagen, gelatin films with a thickness of 0.1 mm were used. IR absorption spectra were produced using the FT-IR spectrometer TENSOR-37 (BRUKER, Germany). In our research ageing resistance of leather was determined by oxidation in the copper ion – hydrogen peroxide system during 10 days. The shrinkage temperature and physical-mechanical properties of the specimens were determined before and after oxidation. Leather after sumac tanning was more resistant to ageing than leather after mimosa tanning. The investigation enables to draw a conclusion that sumac has quite good tanning properties, which allow its usage for process of combined tanning. Developed technology could be used producing ageing resistant leather.

Keywords: sumac, combined tanning, ageing resistance.

INTRODUCTION

Tannins of sumac, or scumpia, are made from the leaves of shrubs of the genus *Rhus Coriaria*, the genus being native to southern Europe and Mediterranean (Greece, Cyprus, Turkey, Bulgaria, Croatia, Monte Negro, Italy) [1]. The history of sumac as a tannide dates back to many centuries ago. The ancient Egyptians and used sumac as a wool dye and later as vegetable tannin. In the Middle Ages sumac was cultivated by the Arabs of Palestine. It is the sumac extract that made colored tanned leather from Morocco and Cordova (known as cordovan) valuable and popular. While in the USSR, Ukraine was the leader in laying-in of sumac tannins [2]. In this country sumac bushes are wide spread in the Crimea and the Black Sea region.

Scumpia has three names: *scumpia vulgaris*, *scumpia coggygia* and sumac dye. Scumpia has long since been used in medicine. Scumpia yields tannin and gallic acid, which are raw materials for producing medicines for hemorrhage, diarrhea, ulcer, edema, throat and skin diseases [1]. In the Mediterranean areas the fruit of scumpia is used as a spice.

Sumac tannins belong to hydrolyzed tannins, gallotannin family. Compared to other tanning agents they have very high sensitivity to heat and decompose to form gallic acid. In [3] a derivative of gallic glucoside was reported to be the main component of sumac tannins, which was revealed by IR-spectroscopy.

The leaves of sumac contain nearly 30% tannin. Besides, they contain gallic acid, glucose, chlorophyll and inorganic salts. According to [4] the leaves should be harvested in mid July, when the content of tannin is maximum. The leaves should be dried at a temperature of 35°C. The optimum conditions of tannin extraction are 60°C and pH of water 3.4-4.6.

Leather tanned with sumac tannin is light, soft. It has pleasant feel and smooth grain. Such leather is well dyed with both anionic and basic dyes. It has high light-, oxidation- and sweat resistance, the antioxidation properties being due to gallic acid. In [5] the

authors suggested that sumac tannins should be used for tanning pig skin. Raw hides were treated with sumac tannins to produce garment leather [6]. The sumac extract was sulfitized with 1% sodium sulfite and 1% sodium hydrosulfite before use. The consumption of 10% sumac tannins and 4.5% synthetic Rotanin-M tan provides producing high-quality leather with a shrinkage temperature of 85%.

The aim of this work is to produce leather with high working properties in combined tanning of hides with sumac tannins and aluminum compounds and pretreatment with phosphonium compounds. The research is of current interest because of the necessity to extend the range of vegetable tannins which increase oxidation resistance of the hides.

OBJECT AND METHODS

The method of combined tanning with THPS and sumac tannides was developed using pelt (thickness – 2-2.2 mm), which was produced from calf skin under conventional technology.

To prepare the hides for vegetable tanning, phosphonium compounds (2-3%) were used instead of chromium compounds and emulsification. The consumption of tannins was 10% of the hide mass. The consumption of aluminum compounds was changed from 1 to 5% (for Al₂O₃).

The control was leather produced according to conventional technology of leather to prosthesis. This technology provides chroming with chromium compounds (0.5% Cr₂O₃), treatment by emulsion of fatliquoring materials and vegetable tanning (10% tannins mimosa or sumac). The amounts of materials used in experiments of this research are presented in percent of pelt mass.

All materials used in leather processing were commercial grade. THPS (commercial name Granofin FCC) were provided by Clariant. This preparation has such advantages as fine tanning properties, low toxicity, high biodegradability and absence of metals. After tanning with phosphonium compounds leather with high ageing and sweat resistance can be produced [7].

IR-Spectroscopy

IR-spectroscopy was employed to investigate the nature of interaction between the tannides and collagen. As a model of collagen, gelatin films with a thickness of 20 μm were used. To produce the films, tannide solutions with a concentration of 50 g/l were introduced into 4% acetic solution of gelatin at 35°C. The tannide consumption was 10% of the collagen mass. The obtained solution was poured onto a Teflon tray and dried until the film is formed at a temperature of 20-22°C. IR absorption spectra were produced using the FT-IR spectrometer TENSOR-37 (BRUKER, Germany). Spectra were interpreted using the tables of characteristic absorption frequencies for different atomic groups [8] and literary sources.

Physical Testing of Leather

The shrinkage temperature (Ts), which shows the hydrothermal stability of leather, was determined using a standard shrinkage meter. Qualitative indexes of leather (tensile strength, relative elongation), pH and amount of Cr₂O₃ in the solution were established using conventional methods.

Investigation of Leather Ageing Resistance

For studying ageing of leather different methods are used: long storage, exposure to mould, oxidation, sun or ultraviolet radiation. In our research ageing resistance of leather was determined by oxidation in the copper ion – hydrogen peroxide system proposed in [9-10]. The leather specimens were treated with 3% hydrogen peroxide solution containing $5 \cdot 10^{-4}$ M copper sulfate for 10 days. After each treatment the shrinkage temperature of the leather was determined. Besides, physical-mechanical properties of the specimens were determined before and after oxidation. By comparing the original physical-mechanical properties and chemical composition of leather produced by different methods of combined tanning with the corresponding characteristics obtained after oxidation with hydrogen peroxide the ageing resistance was evaluated.

RESULTS AND DISCUSSION

Fig. 1 shows IR-spectra of gelatin films treated with vegetable tannides of pyrocatechin (mimosa tannides) and pyrogallol (sumac tannides) groups. The vegetable tannins sumac and mimosa differ in their chemical structure. Unlike mimosa tannins, sumac tannins contain carbonyl groups. As it can be seen in the Figure the spectra of these tannins differ in the low-frequency region ($1500-600 \text{ cm}^{-1}$). In contrast to the spectrum of gelatin-mimosa, the spectrum of gelatin treated with sumac tannins shows an increase in the half-width of band at 1200 cm^{-1} and in optical density at 1032 cm^{-1} for sumac, which can correspond to asymmetrical and symmetrical vibrations of the O=C-O- group of the aromatic compounds or to valence vibrations of the C-OH bond (phenol). Besides, distinct bands with a vibration frequency of $1360 \dots 1400 \text{ cm}^{-1}$ appear, with the overtone at 1700 cm^{-1} , which must be due to in-plane deformation vibrations of associated –OH groups.

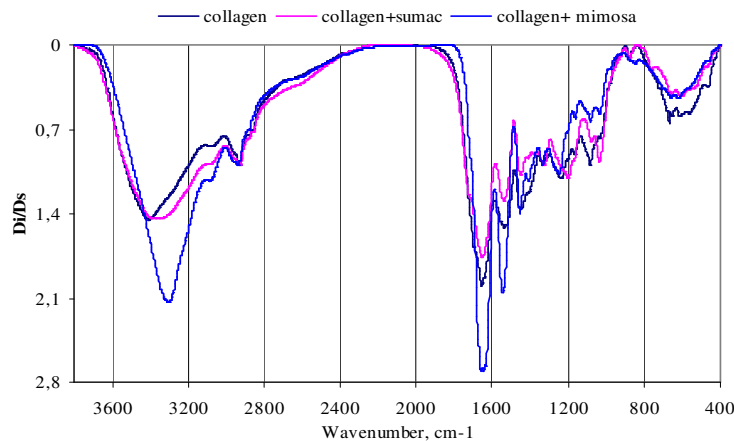


Figure 1. The results of IR-spectroscopy for collagen before and after tanning

For cellulose and its derivatives a well-pronounced band at 1161cm^{-1} is observed, which relates to asymmetrical valence vibrations of the C-O-C bridge [11]. Unlike starting gelatin and that treated with mimosa tannins, in the spectrum of gelatin treated with sumac tannins the absorption at 1162 cm^{-1} is absent, which may result from the C-O-C group being involved in the interaction with collagen or hydrolysis of sumac tannins to form gallic acid.

Thus, a conclusion can be drawn that the interaction of mimosa tannins involves formation of hydrogen bonds between the phenol hydroxyl groups of tannins and amine groups of derma collagen, whereas the interaction of sumac tannins involves both formation of hydrogen bonds between the phenol hydroxyl groups of tannins and amine groups of derma collagen and formation of co-ordination bonds between the carbonyl groups of tannins and derma collagen.

The shrinkage temperature of the semi-finished item after the treatment with phosphonium compounds was $78\text{-}80^\circ\text{C}$, which is sufficient for shaving and splitting in manufacture conditions. In the case of mimosa tannins the liquor of tannins was practically exhausted. The liquor of sumac was far less exhausted, which can be due to a higher content of insoluble substances.

The treatment by aluminum compounds was carried out after draining THPS and vegetable tannins solution. Duration of treatment was 2 h. Sodium hydro carbonate was used to increase basicity reaching solution pH 3.8-4. The obtained leather was neutralized, fatliquored and dried. Qualitative indexes of leather are presented in Table 1.

Table 1. Physical-mechanical properties of the leather

Variant	Tanning agents	Consumption, %	Shrinkage temperature, $^\circ\text{C}$	ΔT_{3B} , %	Tensile strength, N/mm^2	Relative elongation, %	Air permeability, $\frac{\text{cm}^3 \cdot \text{h}}{\text{cm}^2}$	Porosity, %
K1	Mimosa	10	106.0	66.0	17.9	94.5	1665.5	56.8
	Cr_2O_3	0.7	34		–	–		
K2	Sumac	10	97.0	50.5	16.0	70.5	1369.4	51.6
	Cr_2O_3	0.7	48		3.3	25.0		
1	Mimosa	10	104.0	69.2	14.0	76.5	1952.1	58.0
	Al_2O_3	1.0	32		–	–		
2	Sumac	10	84.0	39.2	13.4	68.5	2005.3	58.1
	Al_2O_3	1.0	51		6.7	100.0		
3	Mimosa	10	107.0	65.4	12.4	78.0	1478.8	56.7
	Al_2O_3	2.0	37		–	–		
4	Sumac	10	87.0	39.0	13.7	75.0	1394.3	56.3
	Al_2O_3	2.0	53		10.7	90.0		
5	Sumac	10	96.0	47.9	13.7	78.5	1774.6	63.9
	Al_2O_3	3.0	50		–	–		
6	Sumac	10	106.0	54.7	13.1	71.0	1900.4	60.0
	Al_2O_3	5.0	48		2.1	10.0		

Note. Parameter value before (numerator) and after (denominator) the treatment by hydrogen peroxide.

As it is seen from the given data, the hides treated with mimosa tannins have a higher shrinkage temperature (104-107°C) than those treated with sumac tannins (88-87°C) at the same consumption of aluminum compounds. After tanning the hides were treated with aluminum compounds to increase their thermal resistance. With increasing the consumption of aluminum compounds an increase in the shrinkage temperature of hides treated with sumac tannins is observed up to 106°C. A consumption of aluminum compounds of 3% provides producing leather similar to that pretreated with chromium compounds. Preshaving the hides can enhance the uniformity of tanning with sumac and increase the shrinkage temperature.

The shrinkage temperature of the leather tanned with sumac tannin after the treatment with phosphonium compounds is 96.0°C, the tensile strength is 13.7 N/mm², relative elongation at stress (9.8 N/mm²) is 64.0%. That is by elastic and mechanical properties the leather complies with the State Standard of Ukraine for yuft (with a tensile strength of no less than 12 N/mm² and elongation at stress 9.8 N/mm² of no less than 60%).

Physical-mechanical properties of the leather depend on its chemical composition. Table 2 shows data on the chemical composition of the leather. As it is seen from the data, hides treated with sumac tannins contain more inorganic compounds than those treated with mimosa tannins, which must be due to impurities in the sumac tannin. Besides, with increasing the consumption of aluminum compounds the content of inorganic substances generally increases. The content of substances extracted by organic solvents in the hides treated with sumac tannins does not vary. The overall content of water-soluble substances is higher for the sumac-treated hides than that for mimosa-treated hides probably because of a high content of insoluble substances in sumac, which is due to the method of its production. Besides, with increasing the consumption of aluminum compounds there is observed an increase in the amount of water-soluble substances, which is absolutely logical.

Table 2. Physical-chemical properties of the leather

Index	Variant							
	K1	K2	1	2	3	4	5	6
Shrinkage temperature, °C	106.0	97.0	104.0	84.0	107.0	87.0	96.0	106.0
Content in the leather, %								
– mineral substances	3.7	3.8	3.7	3.9	3.5	4.0	7.1	7.3
– substances, which are extracted by organic solvents, %	8.9	6.5	6.7	6.9	7.2	6.0	7.5	7.3
– general water wash out substance	2.5	2.6	2.2	4.0	4.0	4.7	6.9	6.9
pH of leather	4.3	4.3	5.3	4.0	3.8	3.8	3.7	3.6

Change in the properties of the leather after artificial ageing was determined from the change in shrinkage temperature and physical–chemical indicators (Table 1). Analysis of the results shows that in oxidation there occurs a decrease in the shrinkage temperature and strength limit of the semi-finished item, which comes as evidence of its

partial untanning. In contrast to specimens treated with mimosa tannins, where the shrinkage temperature decreased to 66.8%, the shrinkage temperature of the specimens under study treated with sumac tannins decreased on the average by 45.2%, which is lower than that for the control specimen (50%). Increasing the amount of aluminum compounds for tanning, the oxidation resistance of leather deteriorates. This is likely to be explained by increasing amount of free acid in the derma structure, which is also proved by the pH of chlorine-potassium extract.

After oxidation the leather whose tanning involved 10% sumac tannins and 1-2% aluminum compounds (for Al₂O₃) had a higher strength limit (on the average 8.7 N/mm²) than the control specimens (3.3 N/mm²), which proves their higher ageing resistance. This must be explained by the mechanism of tanning.

CONCLUSIONS

1. A conclusion was drawn from the analysis of physical-chemical properties of the vegetable tannin sumac that it has rather high soundness and satisfactory tanning properties, and therefore can be used for tanning leather.

2. Leather whose tanning involved 10% sumac tannins and 1-2% aluminum compounds (for Al₂O₃) shows better stability with time, which is apparently due to the mechanism of tanning.

3. IR-spectroscopy showed that the interaction between sumac tannins takes place by both hydrogen bonding between the phenol hydroxyl groups of tannins and amine groups of derma collagen and formation of co-ordination bonds involving the carbonyl groups of tannins.

4. The technology proposed is more environmentally friendly as it does not involve chromium compounds in leather manufacture, but uses biodegradable substances. Besides, extraction of sumac tannins does not require cutting off trees, which has a favourable influence on the environment.

REFERENCES

- Bertnet, R. (2001), "Alcuni punti di vista teorici sui tannini in generale", Gambier, Mirabolano, Tara e Sommacco, *Cuoio, Pelli, Materie Concianti*, 77(4), 159-165.
- Mezheninov, M.Yu., Krasnukhin, M.N., Yegorov, B.A. (1962), "Manufacture of Vegetable Tanning Extracts" *Rostekhszdat Publishing House*, Moscow [in Russian].
- Durio, E., Catino, A., Danieni, E. (1961), "Contributo alla conoscenza dei componenti il sommacco" (Nota 4.), *Cuoio, Pelli, Materie Concianti*, 37(2), 61-70.
- Opačić, I. (1972), "Kemijska i tehnološka svojstva tanina iz lišća domaceg ruja. (*Rhus cotinus* L.)", *Glasnik za Šumske pokuse*, Vol.16 (1), 5-104.
- Berislav, G. (1960), "Primjena rujevog ekstrakta kod prerade svinjskih koža", *Koža I obuća*, 9(3), 73-77.
- Tyl, H. (1963), "Garbowanie skór sumakien produkcji krajowej", *Przege. skórzaney*, 18(3), 61-62.
- Downward, B.L., Talbot, R.E., and Haack, T.K. (1997), "Tetrakis(hydroxymethyl)phosphonium Sulfate (THPS), a new Industrial Biocide with Low Environmental Toxicity", *Proceeding of International Conference Corrosion-97*, NACE International, Houston (TX).
- Nakhani, K. (1965), *Infrared Spectra and Structure of Organic Compounds*. Mir Publishing House, Moscow (in Russian).
- Deasy, C., Sister, M. (1965), "A Study of the Oxidative Degradation of Gelatin and Collagen by Aqueous Hydrogen Peroxide Solutions", *Journal of the American Leather Chemists Association*, 60(11), 665-674.
- Deasy, C. (1967), "Degradation of Collagen by Metal Ion-Hydrogen Peroxide Systems", *Journal of the American Leather Chemists Association*, 62(4), 258-269.
- Bycles, N., Segal, L. (1974), *Cellulose and its Derivatives*, I, Mir Publishing House, Moscow (in Russian).