**ECOLOGICAL APPROACHES FOR PROTECTING AND PERFUMING
NATURAL SHEEPSKIN FUR**

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Fur and leather have been among the first materials used for clothing and bodily decoration. It is known that *Homo sapiens* and *Homo neanderthalensis* used fur clothing. Even though the invention of inexpensive synthetic textiles for insulating clothing led to fur clothing falling out of fashion, fur is still worn in most cool climates around the world such due to its superior warmth and durability. In addition, a huge number of furs exists in the ethnography and anthropology museums around the world. The storage and conservation of furs, old and modern, is still challenging for both conservators and population because most commercial products are highly toxic for humans and environment. We therefore tried to control or limit the damage caused by external factors and insects by using green finishing and maintenance treatments. It is known that essential oils, known for their special perfume, can be used to repel insects. Mint, cedar, lavender oils were hence tested to treat sheepskin furs as a final finishing operation. In addition, the use of new products based on natural oils, ethyl alcohol, nonionogenic surfactants from the class of polyethoxylated fatty acids and of polyethylene glycols, and cationic surfactants (quaternary ammonium salts) were tested and proved they contribute to both perfuming and improving the resistance of furs to moths.

Keywords: green conservation, fur, finish & maintenance

INTRODUCTION

In order to prevent the emergence and growth of microorganisms, biocides are used in various stages of leather processing, improving resistance to biological attack and preventing deterioration of mechanical and chemical properties of leathers and furs.

Some biocides used in the leather industry have a certain toxicity, and are prohibited by the directives in force (Directive 2010/75/EU).

The storage and conservation of furs, old and modern, is still challenging for both conservators and population because most commercial products are highly toxic for humans and environment.

Essential oils are very concentrated in active chemical elements (aliphatic and aromatic hydrocarbons, alcohols, aldehydes, esters etc.) and have various properties: they are antiseptic, antibacterial etc. (European Pharmacopeia, 2005).

It is known that essential oils, known for their special perfume, can be used to repel insects (Niculescu *et al.*, 2015; Niculescu *et al.*, 2019).

Mint, cedar, lavender oils were tested to treat sheepskin furs as a final finishing operation. In addition, the use of new products based on natural oils, ethyl alcohol, nonionogenic surfactants from the class of polyethoxylated fatty acids and of polyethylene glycols, and cationic surfactants (quaternary ammonium salts) were tested and proved they contribute to both perfuming and improving the resistance of furs to moths.

The paper presents methods of obtaining the furs fragrant and moth-resistant furs, can be used for preservation of modern and old furs in the museums of ethnography and anthropology.

EXPERIMENTAL

Materials

Mint oil (Adams, Romania), containing menthol – 40.16 %, L-menthone – 23.90%, I-menthone – 14.89%, D-limonene – 8.65%, menthyl acetate – 4.39% etc.

Cedar essential oil (Solaris Plant, Bucharest), containing thujopsene – 37.36%, cedrenol – 20.90% cedrene – 20.14% and cuparene – 9.58%.

Lavender oil (Adams, Romania), containing linalool – 36.59%, linalyl acetate – 35.76 %, alpha – terpineol – 7.63%, lavandulyl acetate – 2.98%, caryophyllene – 2.96%.

Ethanol (Chemical Company, Germany), colorless liquid, boiling point 78.37°C, density -0.79g/cm³;

Nonionic emulsifier – lauryl alcohol ethoxylated with 7 moles of ethylene oxide (Elton Corporation, Romania), density – 0.97 g/cm³ at 40°C, pH (10% solution) – 7-8.

Polyethylene Glycol 400 (Merck, Germany), density - 1.15 g/cm³ at 20°C, flash point > 200°C; pH (10% solution) – 5-7; melting point - 5°C, ignition temperature - 360°C.

Hexadecyl-trimethyl ammonium bromide (Merck, Germany), water solubility of 3g/L, pH (10% solution) – 5-7, melting point 237-243°C, hygroscopic.

Product P-MCL based on essential oils (mint, cedar, lavender): dry substance – 19-21%, pH (10% solution) – 4.5-5.0, density –0.890-0.900 g/cm³.

Sheepskins tanned with syntans based on phenolsulphonic acids and aromatic oxisulfones (INCDTP – Division Leather and Footwear Research Institute Bucharest, Romania).

Methods

Synthesis of materials based on plant extracts for treatment of furs was conducted in a glass flask using a heating and homogenization installation (Velp) and an ultrasonic bath (Elmasonic S 15 H).

Analysis of the essential oils was carried out by using Gas Chromatography Mass Spectrometry Analysis - Agilent 7890 A GC System equipped with Agilent 5795 C MS, and HP-5 MS (0.25 mm x 30 m i.d., film thickness 0.25).

Attenuated Total Reflectance Fourier transform infrared spectroscopy measurements were run with a Jasco instrument (model 4200), in the following conditions: wavenumber range – 600-4000 cm⁻¹; data pitch – 0.964233 cm⁻¹.

Chemical characteristics of products based on essential oils were determined according to the following standards: dry substance (%) – SR EN ISO 4684:2006; pH – SR-EN ISO 4098: 2006.

Chemical and mechanical characteristics of furs were determined according to the following standards: volatile matter % – SR EN ISO 4684:2012, extractible substances % – SR EN ISO 4048:2002, ash % – SR EN ISO 4047:2002, shrinkage temperatures (°C) – SR EN ISO 3380:2003, the longitudinal and transverse tensile strength – SR EN ISO 3376:2012.

Obtaining the Product Based on Essential Oils

The following components were added to the mixing vessel: 20% mint essential oil, 20% cedar essential oil and 20% lavender essential oil, 10% ethyl alcohol, 10% lauric

alcohol ethoxylate with seven moles of ethylene oxide, 10% polyethylene glycol 400, 1% hexadecyltrimethylammonium bromide and deionized water. Components were homogenised using a mechanical stirrer, on an electrically heated installation, at the temperature of 30-35°C, for 15-20 min. In order to homogenise components, an ultrasound bath was used, in which the glass flask was inserted, at the temperature of 25°C, for 10 minutes. The products obtained were marked P-MCL.

RESULTS AND DISCUSSION

Characterisation of Components Used to Obtain P-MCL Product

Mint, cedar and lavender essential oils used to obtain product P-MCL were analysed using GC-MS. Identification of compounds in their composition is presented in Tables 1-3.

Table 1. Identification of organic compounds in the mint essential oil by GC-MS

No.	RT	Amount, %	Compounds
1	17.99	8.65	D-limonene
2	25.33	23.90	L-menthone
3	25.93	14.89	I-menthone
4	26.79	40.16	Menthol

Table 2. Identification of organic compounds in the cedar essential oil by GC-MS

No.	RT	Amount, %	Compounds
1	36.85	20.14	Cedrene
2	37.67	37.36	Thujopsene
3	40.76	9.58	Cuparene
4	45.12	20.90	Cedrenol

Table 3. Identification of compounds in the lavender essential oil by GC-MS

No.	RT	Amount, %	Compounds
1	21.54	36.59	Linalool
2	25.32	7.63	Alpha -Terpineol
3	28.62	35.76	Linalyl acetate
4	29.98	2.98	Lavandulyl acetate

FT-IR Characterization of Components Used and the Obtained Product

Figure 1 presents the spectral characteristics of mint (MIN), cedar (CED), lavender (LAV) essential oils and of product (P-MCL).

a - The FTIR spectrum of MIN

b - The FTIR spectrum of CED

<https://doi.org/10.24264/icams-2020.II.20>

c - The FTIR spectrum of LAV

d - The FTIR spectrum of P-MCL

Figure 1. The FTIR spectra of mint (MIN), cedar (CED), lavender (LAV) essential oils and of product (P-MCL)

The main bands of product P-MCL are (Fig. 1d): 3354 cm^{-1} – indicating the presence of hydroxyl groups, 2961 cm^{-1} , 2924 cm^{-1} and 2872 cm^{-1} – indicating the presence of aliphatic CH_2 groups, 1738 cm^{-1} and 1709 cm^{-1} – indicating the presence of $\text{C}=\text{O}$ group from ester, 1088 cm^{-1} , 1048 cm^{-1} and 881 cm^{-1} given by the $\text{C}-\text{O}$ group from ether.

The bands with similar wavelengths are found in the FTIR spectra of the essential oils of mint, cedar and lavender (Fig. 1a-c), which are part of the composition of the P-MCL perfume product.

Physical-Chemical Characteristics of the Product Based on Essential Oils

The physical-chemical characterization of new P-MCL product, based on essential oils, ethyl alcohol, non-ionogenic surfactants from the category of polyethoxylated fatty alcohols and polyethylene glycols and water: it is a yellowish white fluid, homogenous, with 19-21% dry substance, pH – 4.5-5.0, density -0.890-0.900 g/cm^3 .

FT-IR Characterization of Obtained Fur Assortments

Figure 2 presents the spectral characteristics of the untreated fur with P-MCL, F1 (control sample), (Fig. 2a), compared with those of the treated ones (with P-MCL product) F2, F2(1), F2(2) and F2(3), (Fig. 2b-e). Figure 2f presents superposed IR spectra of treated fur samples with P-MCL product, F2, F2(1), F2(2) and F2(3), which have different intensities, depending on the amount of P-MCL product used.

Figure 2. The FTIR spectra of samples F1, F2, F2(1), F2(2), F2(3)

The main spectral bands of the F1 fur sample are found in the following regions: 2925 and 2874 cm^{-1} (-CH₃, -CH₂-), 1630 cm^{-1} (-OC-N), 1518 cm^{-1} (NH), 1447 cm^{-1} (CH), 1284 and 1235 cm^{-1} (NH-CO), 1144 and 1103 cm^{-1} (CO) (Fig. 2a).

The main spectral bands of the F2 fur sample, treated with the product P-MCL, are found in the following regions: 2965 and 2927 cm^{-1} (-CH₃, -CH₂-), 1636 and 1634 cm^{-1} , characteristic for the groups C = O and -OC-N, 1440 cm^{-1} (CH), 1239 cm^{-1} (NH-CO) (Fig. 2b).

Modification of the F2 fur sample spectral bands was observed at the absorption peaks of approximately 1413 and 1379 cm^{-1} (indicating the presence of C-OH group from alcohol), 1084, 1048 and 881 cm^{-1} (given by the CO group from ether); they are slightly modified and of lower intensities, but are present in the P-MCL product. The above differences between the IR spectra of the treated and untreated fur can be considered as a proof of the presence of the P-MCL product.

Characterization of Furs by Physical-Chemical and Physical-Mechanical Analyses

The values of the physical-chemical characteristics of the furs are comparable to the values set by the standards for sheep furskins intended for clothing (volatile dermal matter 12.20-12.80% and volatile wool matter 10.20-12.60%, extractable dermal substances 9.50-11.70% and wool extracts 0.60-0.90%, ash 3.50-3.90%, pH of aqueous extract, 4-4.5. Values of shrinkage temperatures for sheep furskins are lower (70-75°C) than those of sheep furs processed with basic chromium salts (approx. 80°C).

The longitudinal tensile strength tests resulted in a value of 250-350 N/mm, compared to the standard for the sheep furskins tanned with chromium salts for clothing, which are of min. 110 N/mm, and the transverse tensile strength values are 200-250 N/mm, compared to the values given in the standard for sheep furskins tanned with chromium salts for clothing, which are of min. 80 N/mm.

Characterisation of Obtained Fragrant Fur Assortments

The obtained P-MCL product can be applied to Merinos sheep fur (free of metals). In order to obtain the perfuming effect, the sheep furs were finished with a wetting solution for the final treatment of the furs, using the P-MCL product in different proportions, as follows:

- Sample F2 treated with a solution containing 300 mL/L P-MCL product, 3 mL/L nonionic emulsifier and deionized water (at a temperature of 30°C);
- Sample F2 (1) treated with a solution containing 250 mL/L P-MCL product, 2.5 mL/L nonionic emulsifier and deionized water (at a temperature of 30°C);
- Sample F2 (2) treated with a solution containing 200 mL/L P-MCL product, 2 mL/L nonionic emulsifier and deionized water (at a temperature of 30°C);

<https://doi.org/10.24264/icams-2020.II.20>

- Sample F2 (3) treated with a solution containing 100 mL/L P-MCL product, 1 mL/L nonionic emulsifier and deionized water (at a temperature of 30°C).

The wetting solution is spread evenly over the hair coating, using thick plastic brushes. After depositing the solution, it is uniformized by brushing with plush pad (avoiding staining the dermis with the wetting solution). The operation is repeated twice.

Fur articles treated with a solution containing 300 mL/L P-MCL are more effective (fragrance lasts for 10-15 days).

CONCLUSIONS

- Sheepskins were tanned (free of metals) with syntans based on phenolsulphonic acids and aromatic oxisulfones, and treated with fragrance products based on vegetable extracts with insecticidal action (mint, cedar, lavender).
- The P-MCL product can be used to treat the surface of finished sheep furskins (free of metals) for perfuming and improving the resistance of furs to moths.
- The fragrant and moth-resistant furs can be used for preservation of modern and old furs in the museums of ethnography and anthropology.

Acknowledgements

These works were carried out with the support of Nucleus Program, TEX-PELVISION 2022, 4N/8.02.2019/Act ad.1/2019, with the support of the Ministry of Research and Innovation, project number PN 19 17 02 01 /2020, and within Program 1 – Development of the national RD system, Subprogram 1.2-Institutional Performance-RDI excellence funding projects, Contract no. 6PFE / 16.10.2018.

REFERENCES

- Council of Europe (2005), *European Pharmacopeia*, vol. II, ESCOP Strasbourg.
- Niculescu, O., Leca, M., Moldovan, Z. and Deselnicu, D.C. (2015), "Research on obtaining products for fragrance and biological protection of natural leathers and furs", *Revista de Chimie (Bucharest)*, 66(12), 1956.
- Niculescu, O., Tonea, R.A. and Tonea, S. (2019), "Insecticidal and perfuming composition for the treatment of natural furs and natural fur articles", OSIM Patent, no. 130692/2019.
- *** (2010), Directive 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on industrial emissions (Integrated Pollution Prevention and Control).