ACTA FACULTATIS XYLOLOGIAE ZVOLEN, 57(2): 81−88, 2015
Zvolen, Technická univerzita vo Zvolene
DOI: 10.17423/afx.2015.57.2.08

THE INFLUENCE OF SELECTED COMPONENTS OF ESSENTIAL OILS ON THE MECHANICAL AND OPTICAL PROPERTIES OF THE LIGNOCELLULOSE MATERIALS

Ondřej Mikala

ABSTRACT

The degradation of cellulose and lignocellulose materials is done by several ways. Some examples could be the hydrolytic cleavage of glycoside bonds, oxidation, photo-oxidation, photolysis and biological attack. The biological attack on cellulose and lignocellulose materials can be caused by bacteria or fungi (moulds). This work is focused on the possibility of using vapours of the selected essential oils or their components to protecting archival materials against biological attacks. Essential oils with the highest bactericidal activity were used. Before use in a real environment, it was necessary to prove whether vapours of these active compounds do not degrade cellulose and lignocellulose materials in the library depositories. For testing of mechanical and optical properties after the exposition in saturated vapours of the active compounds were selected sheets based on the following materials: coniferous sulphate pulp, deciduous sulphate pulp, sulphite pulp, groundwood and pulp for the production of handmade paper.

It has been proven that saturated vapours of 7 compounds, which we had tested, had a negative effect on the mechanical properties especially of groundwood material. Change in optical properties is reflected by slight colour variation with a maximum value of 1.41 when applying mixtures of substances no. 2 (limonene, eucalyptol, ocimene) on the material for production of handmade paper.

Key words: lignocellulose materials, essential oils, bending stiffness, colour difference ΔE^*.

INTRODUCTION

To apply the correct protective mediums and procedures in an effort to rescue historical materials based on cellulose and lignocellulose materials is important to know the following degradation processes. Damage of paper materials occurs by hydrolysis of glycosidic bonds, oxidation, photo-oxidation and photolysis and also may be caused by biological attack of microorganisms (GOJNÝ *et al*. 2014b, ČABALOVÁ *et al*. 2014) During degradation process are monitored correlations between paper properties (optical or mechanical) and structural or microscopic characteristics of materials in the paper (degree change of polymerization of cellulose, increasing the proportion of low molecular weight fractions) (BANSA 2002, CALVINI, GORASSINI 2006, KAČÍK *et al*. 2007, ČABALOVÁ *et al*. 2011a,b, 2013, MILICHOVSKÝ *et al*. 2013).

Among the microorganisms that most frequently attack the paper-based materials include *Aspergillus fumigatus*, *Aspergillus niger* and *Penicillium* genus (ĎUROVIČ *et al*.

2002). In nature, plants prevent from infestation by microorganisms by production of essences (essential oils). Essential oils (EO) are complex mixtures of substances, consisting most often terpenes and derivatives thereof, hydrocarbons, alcohols, aldehydes, ketones and carboxylic acids. The use of EO for protection against microorganisms appears to be an alternative to synthetic fungicidal agents (ČEŠEK *et al*. 2014a, b, GOJNÝ *et al*. 2013, 2014a, c). Antimicrobial effects of EO are associated with hydrophilic and lipophilic properties of EO or rather its components, as they are described in a work by KALEMBA *et al*. (2003). Competitive absorption processes for condensation of water and EO in the pores of cellulose and lignocellulose materials are described in article by ČEŠEK *et al*. (2014). Bactericidal effects of different EO have been demonstrated in several studies (MILADINOVIĆ *et al*. 2012). Bactericidal activity of components EO of eucalyptus was tested by Elaissi et al. (2011). Main constituents of EO were determined eucalyptol, α-pinene, p-cymene and limonene. Mechanism of *Escherichia coli* deactivation using limonene and terpenes from the EO is described by Chueca et al. (2014). Bacteriostatic and bactericidal activity of EO of two kinds of sage (*Salvia officinalis*, *Salvia triloba*), growing in southern Brazil, is devoted to the study of Delamare et al. (2007). Main components of the EO are eucalyptol, camphor, borneol and β- pinene. This study is aimed at investigation the effect of saturated vapour mixtures of five components of essential oils and two pure EO on cellulose and lignocellulose materials. This part of the research was focused on monitoring of mechanical properties (represented by bending stiffness and compressive strength) and changes in optical properties. Verification of saturated vapours of substances from EO on mechanical or optical properties on the paper pad can be further used in the library depositories. This application could reduce the risk of microbial infestation of archival documents.

MATERIALS AND METHODS

Lignocellulose material

In order to best simulate the real printed matter stored in archives, 5 lignocellulose materials which are commonly used in the paper and printing industry, have been chosen for testing (Tab. 1).

Tab. 1 Used cellulose and lignocellulose materials.

SaL	deciduous sulphate pulp from Ružomberok, the beating degree 25 °SR
SaJ	coniferous sulphate pulp from Štětí, the beating degree 25 °SR
Si	sulphite pulp from Biocel Paskov, the beating degree 25 °SR
RP	the raw material for the production of handmade paper from the Velké Losiny, consisting of 60% cotton linters and 40% of pulp of flax, the beating degree from 28 to 29 °SR
DS	groundwood with the addition of 10% of sulphite pulp, as described above

Components of essential oils

Five components of EO and two EO with the highest microbicide effect have been chosen for testing. Microbicide effectiveness was tested on microorganisms *Aspergillus brasiliensis, Penicillium aurantiogriseum ex-niger*, and *Cladosporium cladosporioides*. The chosen components of essential oils and two EO are shown in table 2.

Description of the apparatus

The equipment has been composed from seven desiccators. Was maintained relative humidity 75% inside the apparatus and for this purpose was used saturated water solution of

NaCl. Petri dishes with 2.5 ml of mixture no. 1–7 were prepared and placed into the desiccators. After 40 days of exposure were all the dishes supplemented with next 2.5 ml of fresh mixture thereof. All specimens of cellulose and lignocellulose materials were exposed to saturated vapours of substances no. 1–7 for 40 and 80 days.

Tab. 2 Used components of essential oils and essential oils.

Number of mixture	Components
1	α-pinene, camphene, β-pinene, myrcene
2	limonene, eucalyptol, ocimene
3	linalool, linalyl acetate, camphor
4	α-phellandrene, 1,4-cineole, α-terpinene, cymene
5	γ-terpinene, terpinolene, α-terpineol
6	Lavandula angustifolia
7	Citrus aurantifolia

Determination of mechanical properties

Sheets with basis weight about 400 $g \cdot m^{-2}$ have been prepared from 5 fibrous materials on Rapid-Köthen – Sheet former. The sheets were cut to yield test specimens of size 15 × 100 mm. Thickness of samples was also measured. After 40 days half of the specimens have been removed while the other half of the specimens continued in experiment for the next 40 days.

The bending stiffness of the exposed and comparative specimens was measured by the 3-point method (always at least 10 times) using TIRAtest 26005 equipment. The distance between the supports was set at 50 mm. The bottom part of the specimen is exposed to traction and the upper part to pressure forces. From the deflection curve there has been determined the slope of the linear portion of the curve F/δ ($N \cdot mm^{-1}$) and maximum deflection at the end of the reversible deformation δmax (mm).

Parameters obtained from the deflection curve are used to calculate the bending stiffness T ($N \cdot mm^2$) according to equation 1,

$$T = \frac{F}{\delta} \cdot \frac{l^3}{48} \qquad (1)$$

where F/δ ($N \cdot mm^{-1}$) is the linear portion of the curve and the l is distance between the supports. A standard bending stiffness T_0 ($N \cdot mm^2$) eliminates the influence of different material thickness and she was calculated according to equation 2,

$$T_0 = T \cdot \frac{t_0^3}{t^3} \qquad (2)$$

where t_0 is the standard specimen thickness of 1 mm and t is the thickness of the measured specimen.

Compressive strength – SCT (ISO 9895:2008)

A test piece, 15 mm wide, is clamped between two clamps, mutually spaced 0.7 mm (Fig. 1), which are forced towards each other until a compressive failure occurs. The maximum force is measured and the compressive strength ($kN \cdot m$) is calculated from equation 3.

$$\sigma_C^b = \frac{\overline{F}_C}{b} \qquad (3)$$

where $\overline{F}_C$ (N) is the mean maximum compressive force and b (mm) is the initial width of the test piece.

If required, calculate the compressive index (kN m kg^{-1}) from equation 4.

$$\sigma_C^g = \frac{1000 \times \sigma_C^b}{g} \quad (4)$$

where σ_C^b (kN m) is compressive strength and g (g·m^{-2}) is grammage.

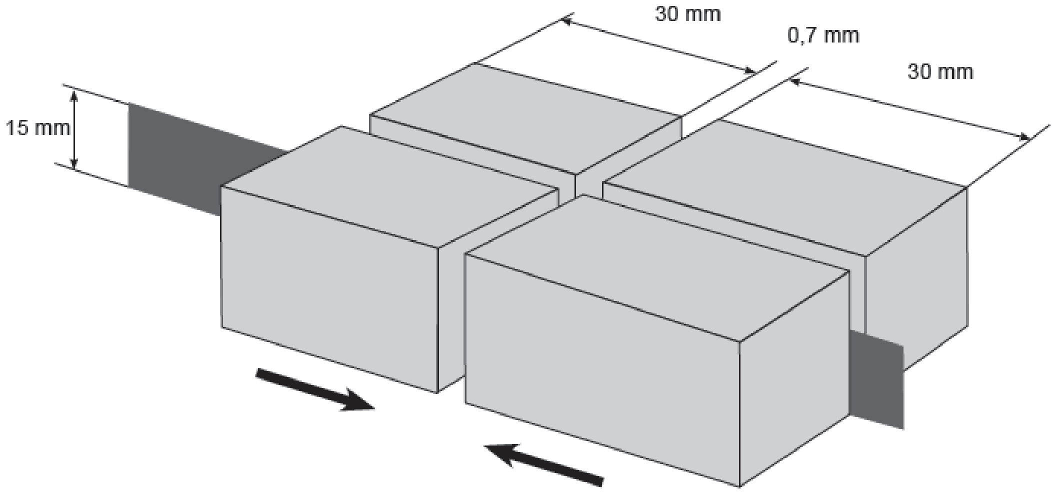

Fig. 1 Compressive strength clamps.

Determination of optical properties:
Optical properties were measured by the spectrophotometer Elrepho Lorentzen & Wettre Company. The specimens were measured (always at least 5 times) before and after exposure to saturated vapours of selected mixtures. The ISO brightness was measured at D65 illumination and L* a* b* coordinates were determined from which the colour difference ΔE* from the unexposed specimen has been calculated (Equation 5) (KAPLANOVA 2010).

$$\Delta E_{ab}^* = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \quad (5)$$

RESULTS AND DISCUSSION

In order to present the rigidity results the standard bending stiffness T_0 was chosen, because it eliminates the influence of the specimen thickness. Figure 2a shows that specimens made of groundwood were more susceptible to saturated vapours. The stiffness of these specimens decreased after 80 days exposure by an average of 41%, no one environment appeared to be significantly destructive. In case of RP materials (Fig. 2b), stiffness increased just slightly by an average of 16%. Data in Fig. 2c and 2d show no significant decrease in rigidity (maximum change was 10%). Due to the significant dispersion of measurements (confidence interval 95%), maintenance of original properties of specimens can be considered. Because of the lack of material specimens of SaJ, measurements were taken only after 80 days of exposure. Figure 2e shows no significant change in stiffness.

Measurement of compressive strength confirmed deterioration of mechanical properties particularly in DS material (Fig. 3a). The material for the production of hand-made paper (Fig. 3b) had decreased compressive index on average by 8% after 80 days of exposure. Mechanical properties of materials Si and SaL (Fig. 3c, 3d) decreased approximately by 12% or more precisely by 15%. A similar decline occurred even in SaJ material (Fig. 3e).

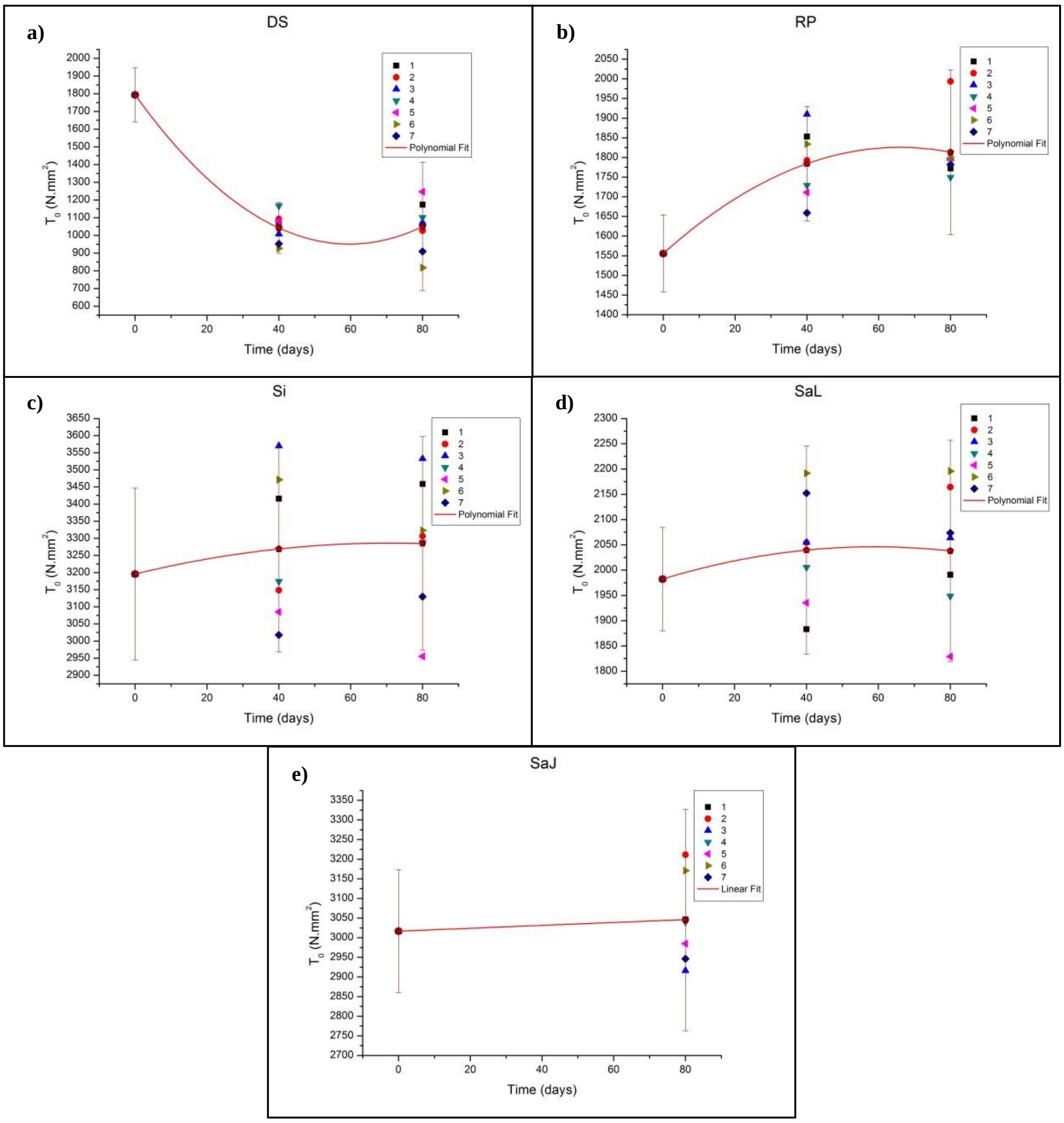

Fig. 2 Dependence of bending stiffness per thickness unit of specimens (DS, RP, Si, SaL, SaJ) on exposure time in saturated vapours substances 1–7.

Optical properties presented by the colour difference ΔE* are listed in table 3. Effect of saturated vapours composed of substances 1–7 appeared on the paper in a colour change only minimally. Highest hue deviation was measured when exposing mixture no. 2, which contained limonene, eucalyptol and ocimene. Colour deviation in this case was the highest in the material for production of hand-made paper but the value of 1.41 can be considered as slight change. Other substances changed the hue of cellulose and lignocellulose materials only negligibly.

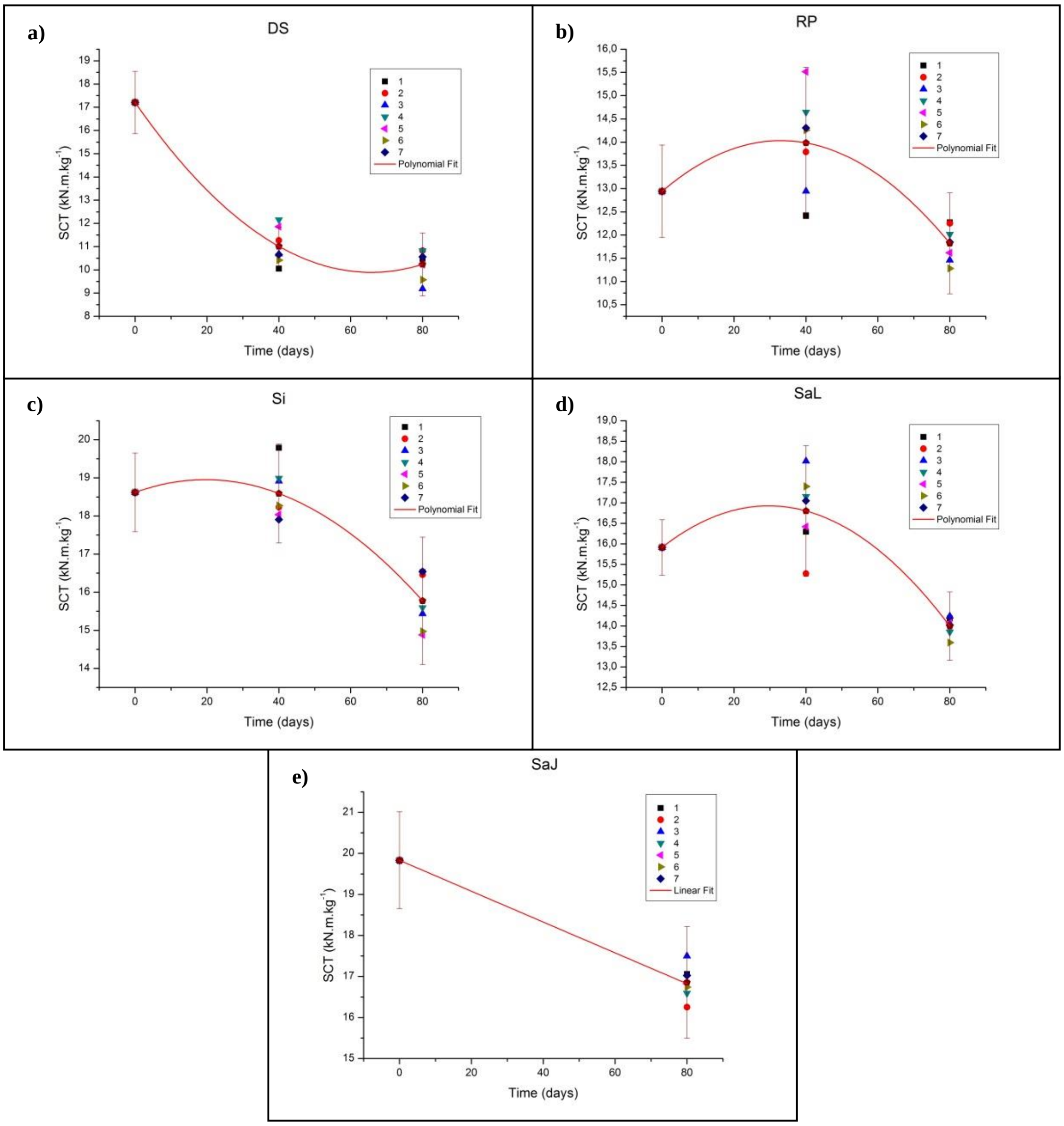

Fig. 3 Dependence of compressive index of specimens (DS, RP, Si, SaL, SaJ) on exposure time in saturated vapours substances 1 – 7.

Tab. 3 Value of colour difference ΔE* after exposure 40 and 80 days.

Number of mixtures	40 days DS ΔE	80 days DS ΔE	40 days RP ΔE	80 days RP ΔE	40 days SaJ ΔE	80 days SaJ ΔE	40 days SaL ΔE	80 days SaL ΔE	40 days Si ΔE	80 days Si ΔE
1	0.45	0.52	0.22	0.70	0.31	0.28	0.13	0.21	0.35	0.64
2	0.52	1.01	0.90	1.41	0.30	0.47	0.66	1.20	0.46	0.89
3	0.20	0.14	0.07	0.10	0.08	0.20	0.17	0.21	0.28	0.32
4	0.16	0.28	0.20	0.27	0.08	0.25	0.10	0.10	0.28	0.31
5	0.30	0.46	0.13	0.31	0.42	0.47	0.03	0.10	0.38	0.45
6	0.25	0.32	0.02	0.04	0.25	0.33	0.17	0.19	0.29	0.42
7	0.22	0.12	0.13	0.06	0.28	0.40	0.17	0.15	0.34	0.48

CONCLUSIONS

This part of the research focused on the effect of essential oils and their components on cellulose and lignocellulose materials is an important part of the project, which aims to protect archival documents. Despite the fact that tested ingredients EO and EO alone have proven bactericidal effects, it is important to find a suitable substance or combination of substances, which also does not affect the paper pad in mechanical, optical and chemical way. It has been proven that saturated vapours of 7 compounds, which we had tested, had a negative effect on the mechanical properties of wood-based material. Stiffness and compressive strength after exposure of saturated vapours decreased approximately by 40%. This significant decline can be attributed to plasticity of fibres and loosening connections among them. In case of other cellulose materials the change of mechanical properties was only about 15%. It is necessary to take into account that the specimens were exposed to saturated vapours, which could not be applied in the library depositories or more precisely they would have to be diluted many times. Change in optical properties is reflected by slight colour variation with a maximum value of 1.41 when applying mixtures of substances no. 2 (limonene, eucalyptol, ocimene) on the material for production of handmade paper. Other saturated vapours did not affect significantly optical properties of paper pads.

For real application EO or their components in the archives with paper artefacts, which threaten to microbial attack, it is necessary to follow up convenient composition of protective vapours and suitable method of application into the space.

LITERATURE

BANSA, H. 2002. Accelerated Ageing of Paper: Some Ideas on its Practical Benefit. In Restaurator, 2002, 23(2): 106–117, ISSN 0034-5806.

CALVINI, P., GORASSINI, A. 2006. On the Rate of Paper Degradation: Lessons From the Past. In Restaurator, 2006, s. 275–290, ISSN 0034-5806.

CHUECA, B., PAGÁN, R., GARCÍA-GONZALO, D. 2014. Oxygenated monoterpenes citral and carvacrol cause oxidative damage in Escherichia coli without the involvement of tricarboxylic acid cycle and Fenton reaction. In International Journal of Food Microbiology 189: 126–131, ISSN 0168-1605.

ČABALOVÁ, I., KAČÍK, F., SIVÁK, J. 2011a. The changes of polymerization degree of softwood fibers by recycling and ageing process. In Acta Facultatis Xylologiae Zvolen, 53(1): 61–64. ISSN 1336-3824.

ČABALOVÁ, I., KAČÍK, F., GEFFERT, A., KAČÍKOVÁ, D. 2011b. The effects of recycling and its environmental impact, In Elżbieta Broniewicz (ed.).: Environmental management in Practice. INTECH, 2011, s. 329–350, ISBN 978-953-307-686-7.

ČABALOVÁ, I., KAČÍK, F., BRIŠKÁROVÁ, A. 2013. Tržná dĺžka a makromolekulové vlastnosti papierov v historických knihách. In Acta Facultatis Xylologiae Zvolen. 2013. 55(1): 61–70. ISSN 1336-3824.

ČABALOVÁ, I., KAČÍK, F., TRIBULOVÁ, T., GOJNÝ, J. 2014. Vybrané vlastnosti historických papierových dokumentov. In Wood, Pulp and Paper 2014, Polygrafia Academica 2014 - WPP a PA 2014. Bratislava: Slovenská chemická knižnica, 2014. s. 265–270. ISBN 978-80-89597-16-1.

ČEŠEK, B., MILICHOVSKÝ, M., GOJNÝ, J. 2014a. Mutual Competitive Absorption of Water and Essential Oils Molecules by Porose Ligno-Cellulosic Materials. In Journal of Biomaterials and Nanobiotechnology. 5(2), ISSN 2158-7027.

ČEŠEK, B., MILICHOVSKÝ, M., GOJNÝ, J. 2014b. Essential Oils Influence upon Chemical Aging Process of Lignocellulosic Materials. In PROGRESS'14 Papers. Łódź : Stowarzyszenie Papierników Polskich, 2014, s. 1–13. ISBN 978-83-60419-08-6.

DELAMARE, A., P., L., MOSCHEN-PISTORELLO, I., T., ARTICO, L., ATTI-SERAFINI, L., ECHEVERRIGARAY, S. 2007. Antibacterial activity of the essential oils of *Salvia officinalis* L. and *Salvia triloba* L. cultivated in South Brazil. In Food Chemistry 100: 603–608, ISSN 0308-8146.
ĎUROVIČ, M. 2002. Restaurování a konzervování archiválií a knih. 1. vyd. Praha : Paseka, 2002, 38–48 s. ISBN 80-718-5383-6.
ELAISSI, A., HADJ SALAH, K., MABROUK, S., LARBI, K., M., CHEMLI, R., HARZALLAH-SKHIRI, F. 2011. Antibacterial activity and chemical composition of 20 Eucalyptus species' essential oils. In Food Chemistry, 129: 1427–1434. ISSN 0308-8146 .
GOJNÝ, J., ČEŠEK, B., MILICHOVSKÝ, M. 2013. Vliv esenciálních olejů na vlastnosti lignocelulózového materálu. In Selected processes at the wood processing [elektronický zdroj] : X. international symposium, September 11-13, 2013, Ružomberok Zvolen. Technical University in Zvolen, 2013. ISBN 978-80-228-2534-4. - CD-ROM, s. 98–108.
GOJNÝ, J., ČEŠEK, B., MILICHOVSKÝ, M., KŘUMAL, K., VEČEŘA, Z. 2014a. Ochrana lignocelulózových materiálů aplikací par esenciálních olejů – posouzení vlivů těchto látek na jejich vlastnosti. In Papír a celulóza. 69(2): 93–97. ISSN 0031–1421.
GOJNÝ, J., MIKALA, O., ČEŠEK, B., ČABALOVÁ, I. 2014b. Distribúcia dĺžky vlákien historických papierových dokumentov. Acta Facultatis Xylologiae Zvolen, 2014, 56(2): 55–61. ISSN 1336-3824.
GOJNÝ, J., ČEŠEK, B., MIKALA, O., MILICHOVSKÝ, M., ČABALOVÁ, I., KŘŮMAL, K. 2014c. Esenciální oleje a pórovité materiály na celulózové a lignocelulózové bázi – ochrana archiválií. In 2. ročník mezinárodní chemicko-technologické konference: sborník abstraktů a plných textů. Praha : Česká společnost průmyslové chemie, 2014, s. 1–5. ISBN 978-80-86238-61-6.
KAČÍK, F., KUČEROVÁ, V., VÝBOHOVÁ, E., KIRSCHNEROVÁ, S. 2007. Hodnotenie starnutia papiera metódou gélovej permeačnej chromatografie. In Acta Facultatis Xylologiae Zvolen. XLIX(1): 27–34. ISSN: 1336-3824.
KALEMBA, D., KUNICKA, A. 2003. Antibacterial and Antifungal Properties of Essential Oils. Current Medicinal Chemistry 2003, (10): 813–829.
KAPLANOVÁ, M. 2010. Moderní polygrafie. Praha : Svaz polygrafických podnikatelů, 2010, 25 s. ISBN 978-80-254-4230-2.
MILADINOVIĆ, D., L., ILIĆ, B., S., MIHAJILOV-KRSTEV, T., M., NIKOLIĆ, N., D., MILADINOVIĆ L., C., CVETKOVIĆ, O., G. 2012. Investigation of the chemical composition–antibacterial activity relationship of essential oils by chemometric methods. Analytical and Bioanalytical Chemistry 2012, 403(4): 1007–1018. DOI: 10.1007/s00216-012-5866-1.
MILICHOVSKÝ, M., ČEŠEK, B., FILIPI, M., GOJNÝ, J. 2013. Cellulose Aging as Key Process of Paper Destruction. In Przeglad Papierniczy. 2013. 69: 291–298. ISSN 0033-2291.

Acknowledgment

This work was created with the support of the Ministry of culture of the Czech Republic in the Project NAKI DF11P01OVV028 "protection of book Fund and the documents application of essential oils."

Addresse of author

Ing. Ondřej Mikala
University of Pardubice
Faculty of Chemical Technology
Institute of Chemistry and Technology of Macromolecular Materials
Studentská 95
532 10 Pardubice
Czech Republic
ondrej.mikala@gmail.com