

Complex Analytical Investigations of Old Wax - sealed Romanian Paper Documents

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Waxes as a component of seals, are recognized in our history as adhesives, for surface coating purposes, modeling or casting materials and also in conservation practice. The waxes with mineral, vegetable and animal origin should be connected to modern methods of analysis, due to their complex composition: long chain hydrocarbons, acids, alcohols, esters. They support many mechanical damages in library and archive collections: cracking, pieces lost by an excessive handling of documents. In this paper the compositional analyses of some wax seals belonging to some paper samples have been achieved by Raman spectroscopy and Fourier transform infrared spectroscopy (FTIR) - for molecular structural information of wax materials, by gas chromatography / mass spectrometry (GC/MS) - for evidence of some compounds resulted from degraded wax seal, and by optical microscopy (OM) and scanning electron microscopy (SEM) - for visualization of the damaging effect on the wax seal. All these analytical investigations have been achieved for wax seals detached from the paper samples recovered from two disaffected pulp and paper factories - Letea and Busteni (Romania) belonging to Romanian industrial patrimony.

Keywords: waxes, FTIR, Raman spectroscopy, GC-MS, microscopy, old paper.

Waxes as translucent solid substances that melt easily, have various source: mineral, vegetable and animal. In general, they contain long chain hydrocarbons, acids, alcohols and esters or mixtures of these [1]. Waxes are known as adhesives, component of seals and as materials in conservation practice [2, 3]. Wax is a mixture of rosin, shellac, turpentine and mineral coloring agents which, because of their plastic properties when heated is used to seal letters, packages, the sealing of the vials [4]. Mountain wax or lignite wax, which is a mineral waxes obtained from brown coal, is a mixture of esters derived from lignite bituminous by solvent extraction. The untreated these products are hard and dark; after refining can be white. Mountain white waxes are used as insulating material, paper impregnation and the manufacture of special paints. Much of the archive seal's damage was caused due to brittleness over time, and excessive handling of documents, which provoke the materials to become opaque and friable [5, 6].

In order to identify the degradation sources, is important to use different concerted analytical techniques. In our research the analyses have been made by Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy, used to identify molecular structural information of waxes and for qualitative characterization of decomposition processes. FTIR can provide molecular structural information of wax materials. The paint cross sections were analyzed using Raman spectroscopy in order to identify pigments and additives. The composition of degraded wax seals was determined using gas chromatography/mass spectrometry (GC/MS). Some compounds with up to 27 carbon atoms are present in

beeswax itself. Also, by different microscopic techniques, the degradation aspects are identified and the eventually impurities and damaging compounds generated during the degradation in time. The work outlined in this paper shows that small amounts of waxes and greases have been encountered in old paper conservation.

Experimental part

Materials

Some paper samples with wax seals from two disaffected pulp and paper factories - Letea and Busteni (Romania) belonging to industrial patrimony, have been studied in this paper. The aspect of the wax seal is shown in figure 1.

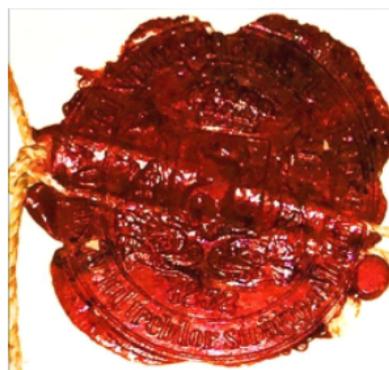


Fig. 1. The aspect of the wax seal from 1852.

Stearin (Stearic acid 50, CAS Number 67701-03-5, tested according to European Pharmacopeia) and paraffin (CAS Number 8002-74-2, European Pharmacopoeia Reference Standard) reference materials were purchase from Sigma Aldrich Co. (Steinheim, Germany).

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Bee wax sample was collected by beekeeper from apiaries and then, the samples were separated by the honey and stored into laboratory at -20°C . The spruce and juniper resins were collected from the Bucegi Natural Park (Dambovita County).

Analytical investigations

The FTIR spectra have been recorded by Attenuated Total Reflectance (ATR) with a Perkin Elmer Spectrum GX spectrometer (PerkinElmer Ltd., UK), in the following conditions: range 4000 cm^{-1} to 580 cm^{-1} , 32 scan, resolution 4 cm^{-1} . Also, some samples have been investigated using Vertex 80 spectrometer (Bruker), with the following parameters: range $8000\text{--}350\text{ cm}^{-1}$ and resolution 0.2 cm^{-1} .

Raman spectra have been obtained with a portable dual wavelength Raman analyzer IR -XANTUS 2 - RIGAKU, with the following parameters: Dual wavelength source 1064 nm & 785 nm , spectral range (cm^{-1}) $200 - 4000$, spectral resolution (cm^{-1}) $7 - 10$, LASER output power (mW) $400 - 490$, LASER output power (mW) $30 - 490$, cooled detectors: CCD and InGaAs. Spectra were acquired using 10 s of signal collection time and five accumulations.

Gas-chromatography with mass spectrometry (GC/MS) has been achieved with GC/MS Triple Quad Agilent Technology (for compounds identification we based on NIST Library). GC method: *Column DB-WAX* ($L = 30\text{ m}$, $D = 250\text{ }\mu\text{m}$, $d = 0.25\text{ }\mu\text{m}$; oven program: 50°C for 5 min , then $4^{\circ}\text{C}/\text{min}$ to 150°C , then $10^{\circ}\text{C}/\text{min}$ to 320°C ; carrier gas: He, flow= $1\text{ mL}/\text{min}$; injector temperature: 250°C ; injection volume: $0.5\text{ }\mu\text{L}$); *MS Method QQQ* Collision Cell: quench flow gas (He) = $2.2\text{ mL}/\text{min}$; collision flow gas (N_2) = $1.5\text{ mL}/\text{min}$; type of source: EI; electron energy: 70 eV ; source temperature: 230°C ; auxiliary temperature 2: 280°C ; scan segment: $40\text{--}400$; type of chromatogram: TIC.

The SU-70 Field Emission - Scanning Electron Microscope (FE-SEM) was used to produce enlarged images of a variety of specimens, achieving magnifications of over $800000\times$ providing high resolution imaging in a digital format. The accelerating voltage (V_{acc}) of SU-70 may vary from 0.1 kV to 30 kV and the resolution is 1 nm (at $V_{\text{acc}} = 15\text{ kV}$) [7-9].

For examination in transmitted light, it has been used a direct microscope Primo Star. It offers the possibility of examining evidence in transmitted light at a magnification of between $4\times$ and $100\times$. Optional equipment can be attached to a digital video camera (Axiocam 105) which, through microscope software allows acquisition of information in real time, both static and moving and conversion from 2D to 3D.

Results and discussions

The FTIR spectra achieved for the investigated samples put into evidence specific groups of the wax composition [10], as follows:

- the bands around 3500 cm^{-1} denote the presence of OH groups, more intense in the juniper sample. The C - H (methyl and methylene) stretching vibrations of saturated hydrocarbons are seen below 3000 cm^{-1} , and for the region of $2800\text{--}3200\text{ cm}^{-1}$, especially;

- the bands from the region $2929\text{--}1456\text{ cm}^{-1}$ are attributed to CH_3 and CH_2 vibrations of hydrocarbonated structures, etheric and alcoholic groups. The same groups could be identified by the bands from 1242 to 1178 cm^{-1} , most probably for the acid resins;

- the main difference is the presence of a peak in region of 1700 cm^{-1} which corresponds to a carbonyl ($\text{C}=\text{O}$) stretching vibration from free carboxylic acid and from esters;

- the observed differences must be related to primarily the flavonoids, diterpenes and triterpene compositions of the resins related to their sources.

In figure 2 it is presented the FTIR spectra of the unknown sample (wax seal compared with paraffin, stearin, and different resins collected from spruce, juniper and bee waxes). In the unknown sample, in the infrared spectrum can be detected bee wax and also the juniper resin.

But, these compounds are easier to be identified by Raman spectroscopy (fig. 3). Some extra peaks that don't belong to bee wax could be identified, belonging to cellulose (1098 cm^{-1}), lignin (1600 cm^{-1}) or to other ingredients present in wax seal, as paraffin, stearin and bee wax. As a partial conclusion, the wax seal contains in majority spruce resin, but also different ratios of juniper, bee wax, paraffin, stearin [10-12].

The black colored seals is a sign of deteriorated due to the presence of the pigments added, which contain metal ions (e.g. lead, copper, iron, mercury). Several hypotheses for the decomposition and brownish coloration circulate, some based on the formation of black $\beta\text{-HgS}$ or of metallic mercury as a deposit. The degraded wax seal may contain artificial cinnabar ($\alpha\text{-HgS}$) which could be transformed into HgCl_2 , as an extremely poisoning compound, able to sublimate [13,14]. The concentration of Hg detected in the wax seal is around % (determined by EDXRF and reported elsewhere [3]).

In order to identify the presence of a coniferous resins, a chromatographic technique has been used in this paper. The fast GC analysis of the slightly more polar constituents of pine resin (fig. 4 a) can be performed in less than 15 minutes with a good resolution for these kinds of diterpenoid isomers. Figure 4b shows the GC/FID analysis of the sample, revealing the presence of common saturated acids. The results are similar with those reported by literature's publications [15].

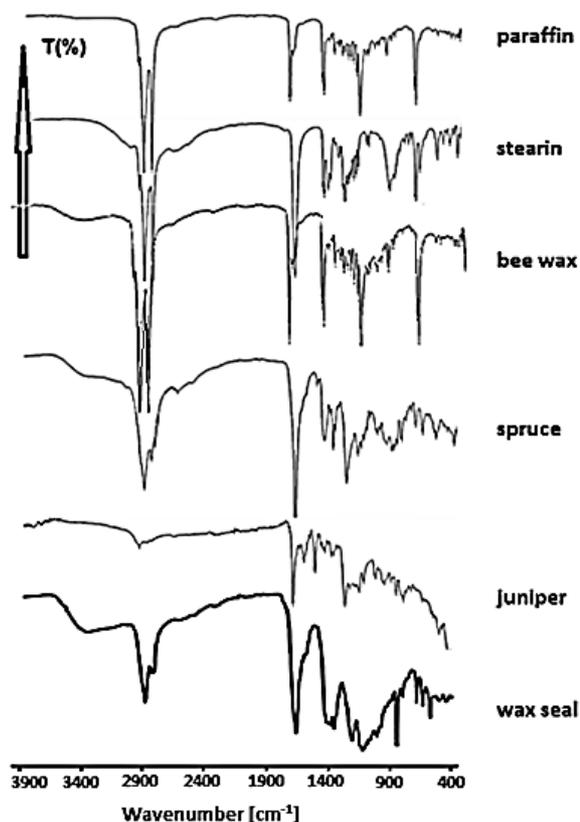


Fig. 2. FTIR spectra of wax seal and the individual resin components

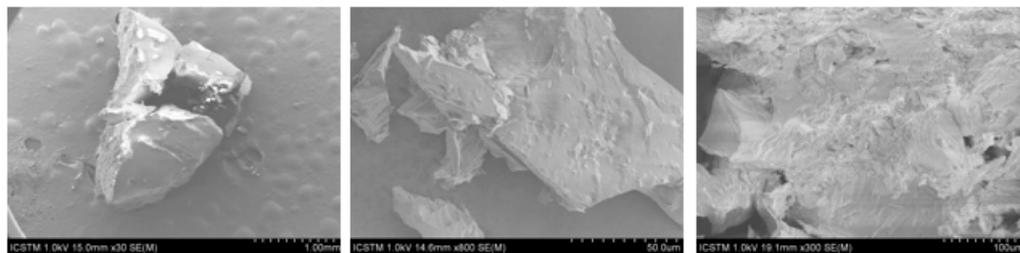


Fig. 6. SEM of wax seal revealing the samples fractures

Conclusions

FTIR and Raman provide general characterization of the waxes containing different organic components and serve to identify coniferous resins, bee wax and organic molecular mixtures. These natural products are mixtures of diterpenoids, long-chain alcohols and fatty acids. By optical microscopy and SEM is possible a direct observation of the black degradation parts, most probably based on Hg and their fractures due to damages supported in time.

Acknowledgements: This work was supported by a grant of the Romanian National Authority for Scientific Research, CNDI-UEFISCDI, projects number 11BM/2014, PNII 261/2014 and PN 16.31.02.04.02.

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Manuscript received: 21.12.2017