INVESTIGATIONS AND CONSERVATION METHODS OF AN HISTORICAL DOCUMENT DEGRADED BY EMPIRICAL INTERVENTIONS

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Abstract

Social factors affect old documents, sometimes their effects being irreversible. This document, with a great historical and documentary value, raised particular problems for the restorative specialist due to an empirical intervention performed at the beginning of the 20th century. Moreover, the document showed numerous ruptures, embrittlement and stains, both on the paper support and on the attached cardboard. Scientific investigations were carried out for identifying the materials with which the empirical restoration was performed, the biological agents which caused the biological attack and measuring the pH values. All obtained results allowed to find the most suitable treatment of preservation of this document.

Keywords: scientific, conservation, document, empirical, interventions

1. Introduction

Object of the present study is an administrative document issued by the Epitropy of the Assets of the Holy Sepulchre, from a particular collection, and it is related to a troubled period in the history of the monasteries on the territory of Romania. This period begun as early as the 16^{th} century, when some rulers, boyars or their descendants have 'dedicated' their foundations to some larger churches in the East and found themselves in difficulty after the Ottoman conquest. The conditions specified in the documents of dedication were: the maintenance of settlements, the fulfilment of all devotionals, the hosting of travellers and visitors, the establishment of hospitals, schools and other charitable and public utility settlements, the care of those wounded in war and aiding the country when needed) [1]. In Moldova, the era of 'dedication' of the monasteries began at the end of the 16th century, during the reign of Petru Schiopu, along with the construction of the Saint Sava Monastery in Iasi, in 1583, with the money of the homonymous monastery in Jerusalem. The Greek monks, who came from there, received from the ruler a place for houses "to live there and build their own church" [2].

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If in the beginning, in the 16th century, the spiritual leadership and the economic administration of the earthly monasteries dedicated to the Holy Places were carried out by Romanian abbots, under the control of the founders, then of their heirs or, in their absence, of the state, during the Phanariote period (1711-1821) the issue of dedication has undergone significant changes. Little by little, Greek abbots appointed as leaders of the monasteries by the Phanariote rulers replaced the Romanians, becoming only masters of their possessions. Often, they robbed the movable and immovable assets of the monasteries, their purpose being to raise as much money as possible [3]. Moreover, the 'dedicated' monasteries came to be in a dreary state and the monastic life was severely weakened. According to an official statistic from 1855, the monasteries in Moldova owned 215 estates, of which 101 were administrated by the Holy Sepulcher, 87 by Mount Athos, 12 by Mount Sinai, 5 by Constantinople, 3 by Alexandria, 2 by Antiocheia and 5 by some monasteries in Greece [4].

The institution that administered the church assets was called Epitropy, an institution led by a council of epitropes (the term *epitrope* was introduced in Romanian language in the 18th century). In Moldova, the administrative seat of the Epitropy of the Holy Sepulchre was at Saint Sava Monastery in Iaşi. 91 documents of the Epitropy of the Holy Sepulchre dating from the period between 1827 and 1861 are kept by the National Archives of Iaşi.

2. Materials and methods

The size of the investigated historical document is of 34.5 x 48.5 cm and is made of industrial paper. On the back, the document was doubled, at a later date, with cardboard. The text of the document was analysed macroscopically, with the magnifying lens and with the ultraviolet lamp, model EL365-254. The composition of the adhesive attached of support was analysed using the DRIFTS technique.

Diffuse Reflectance Infrared Fourier Transform (DRIFT) Spectra were measured using VERTEX 70, Bruker. This instrument was equipped with an EasiDiff diffuse reflectance sampling accessory (Pike Technologies, USA). The spectral measurements have been processed with the Spectra Manager. Normalization of the spectra was based on an internal standard. All spectra were recorded from 4000 cm⁻¹ to 400 cm⁻¹ with 32 scans and spectral resolution of 4 cm⁻¹. The values obtained are transformed to absorbance spectra (log [1/reflectance]).

The pH measurement of the paper and cardboard was performed with a Hanna Instruments electronic pH-meter equipped with temperature sensor and automatic correction of the measured pH value depending on the temperature.

Biological investigations were performed according to the usual protocol, described in a previous paper [5].

3. Results and discussion

3.1. The conservation state of the historical document

The document was widely used and probably kept folded, which led to the appearance of massive cracks and fractures on the folding lines, both longitudinally and transversely (Figure 1). The storage conditions were most certainly inadequate, which led to the severe deterioration of the document. An empirical restoration intervention, a common practice on old books and documents [6, 7], worsened the deterioration processes of the document.



Figure 1. Multiple deteriorations on the investigated historical document: (a) fractures on the folding lines, (b) massive cracks and empirical interventions.



Figure 2. Aspect of biological investigations: (a) sampling area of the document, (b) macroscopic appearance of yeasts of *Saccharomyces* sp. after 14 days from inoculation on culture medium.

The paper shows numerous damages: massive biological attack, deformations, cracks, fractures, detachments of the paper from the cardboard, chromatic changes, loss of ink legibility, stains and numerous deposits of dust and fouled dirt. Strips of paper were observed underneath the cardboard with which the document was doubled during the empirical restoration intervention, which were probably used in an attempt to reinforce the document that was massively fractured in the folding area. Pieces of newspaper applied to consolidate the support paper, were also found.

Unfortunately, these empirical restoration interventions, made with newspaper that quickly became acidic and the use of an adhesive that triggered a powerful microbiological attack, contributed significantly to the deterioration of the document.

3.2. Results of pH measurements

The pH measured at the surface of the document shows acidic values, respectively 4.7-4.9 for paper support and 2.5-3.2 for attached cardboard.

3.3. Biological investigations results

Biological investigations demonstrated the presence of fungal attack (*Penicillium* sp, *Saccharomyces* sp.), especially in areas with empirical restorations (Figure 2).

3.4. Text analysis results and document dating

The document is a standardized form issued by the 'Epitropy of the Assets of the Holy Sepulchre from Moldova', written in capital letters, in Greek. The document was printed at the Buciumul Român typography and is filled in with black typographic ink. The Buciumul Român typography was founded in 1850 by the writer Theodor Codrescu (1819-1894) from Iași, through which he supported the Unification of the Romanian Principalities. On the stamp at the bottom of the page, the following text in Greek can be identified only the left side a part of the text: *Holy Sepulchre 1826*.

The text of the document is composed of two columns: in the lower left there is a text in Greek, and on the right side the same text is translated into Romanian, but written with Cyrillic characters. In the upper half of the document there are texts written with manuscript ink, which in became illegible overtime. At the bottom, on the right side, part of the text in Romanian, written with Cyrillic characters, is legible. From the text written in Greek and in Romanian with Cyrillic characters, it appears that this document represents an act of donation to the Holy Places, with legal regulations and references to the Civil Register. The document was dated using the ultraviolet lamp at the wavelength of 365 nm. This way, the handwriting regarding the year of issuance, on the left side, at the bottom of the document became visible, thus making visible the document date (1859) (Figure 3a).

On the cardboard attached to the back of the document there is a manuscript note, where the following text in Romanian can be deciphered: "This [illegible] is approved According to the application attached to [illegible] reg. [registered] under no. 13/904. Chief of Archive [illegible]." Therefore, the empirical restoration of the document took place before 1904 (Figure 3b).

3.5. Optical and spectroscopic analysis results

The presence of fluorescent stains at the level of the substance used as an adhesive for gluing the cardboard attached to the back of the document was observed following the optical investigation with the UV lamp. For the identification of this adhesive, detachable micro-samples were taken from the document edge and analysed using FTIR spectroscopy, the DRIFT method.

It is observed that under natural light the adhesive between paper and cardboard appears in yellow colour, like other natural aged adhesives. Viewed under ultraviolet light with 365 nm, the back side of a leaf of paper revealed the spots of adhesive who exhibited strong greenish fluorescence (Figure 4), associated with an aged natural resins varnish [8].

It is known that light orange fluorescence can be associated to a natural resin such as shellac [9], but in this case the fluorescence was green. Rivers [10] affirms that the auto-fluorescence of natural resins viewed under UV light appears greenish-white in case of dammar or mastic resins and that aged mastic resin absorbs more of the UV component than fresh dammar resin films.

The natural resins can be divided into three subfamilies: shellacs, diterpenoid resins and triterpenoid resins. The IR spectrum for the adhesive sampled from the investigated document showed peaks consistent with a natural resin based varnish, having a best spectral match to a triterpenoids resin (probably mastic) (Figure 5).

The absence of IR band between 3070 and 3088 cm⁻¹ assigned to the characteristic vinyl group present in diterpenoid permits to conclude that studied adhesive is a triterpenoid resin. The presence of peaks at 2905 and 1641 cm⁻¹ could be attributed to mastic resin, according to literature [11]. A fingerprint region around 1440 and 1160 cm⁻¹ confirm the presence of mastic, even the aging of natural resins cover some detail, as demonstrated in case of FTIR study of varnish layer of icons [12]. Other existing peaks can appear due the particular components of mastic, responsible for its pronounced yellowing predisposition, and less to the disposition to radical oxidative degradation [13].

Mastic is the resin of the wild pistachio from the Sumac family, cultivated from ancient times on the Mediterranean island of Chios. More than 120 chemical compounds were identified in the resin and the major components are a natural polymer, acidic and neutral triterpenes and volatile secondary metabolites [14].

Melniciuc-Puica & Ardelean/European Journal of Science and Theology 16 (2020), 5, 173-180



Figure 3. Results of dating of document with UV light lamp (365 nm): (a) dating the writing document: *1859 feb. 26*, (b) empirical interventions dating: *No 13/904* (before 1904).



Figure 4. Greenish fluorescence observed on empirical restoration area with UV light lamp (365 nm).



Figure 5. FTIR spectra of the adhesive found between paper and cardboard.

Fresh mastic is soluble in polar solvents like alcohols. The literature [15] states that the traditional mastic used in the varnishes of old paintings sometimes dissolves in essence of turpentine, but this solvent is not usual in preserving old paper. Over time, mastic has been known for its benefits such as preventing tooth decay and eliminating fungal infections. This resin can be used in art as an adhesive for old wood [16] and especially as a varnish for old oil painting. It was the principal resin used for varnish painting in nineteenth and twentieth century.

It is observed that this adhesive involved the serious problems of the cleaning operation, the solubility of the adhesive being partial. It is known that portions of resins are soluble in organic solvents, but complete solubility needed moderately polar solvents; by UV photo-oxidation, mastic requires more polar solvents for dissolution [17]. In practice of cleaning the varnish of wood, water can be used to provide the necessary polarity for removing degraded varnish, whilst the addition of a detergent or a small amount of an aromatic solvent can be used to bring non-polar components of degraded natural resin varnish into solution. In this case, the using of water could create the solubilisation of inks used for writing the document. So, the empirical interventions create serious problems on conservation interventions.

3.6. Conservation and restoration interventions

The scientific investigations aimed at identifying the biological agents that caused the biological attack, measuring the pH values, identifying the materials used for the empirical restoration, etc. After the disinfection treatment, a dry cleaning of the document was performed, on both sides. Then cleaning with 5% MC (Methyl Cellulose) gel was performed to remove the adherent deposits from the document surface.

Given that the cardboard had a very acidic pH, it was decided to remove it, as well as the thick layer of adhesive used to glue it. For this purpose, moistened sheets of filter paper were applied to the back of the document, which were changed several times, because once the cardboard became moist, coloured degradation compounds were extracted. After removing the cardboard, the adhesive layer and the strips of paper used during the empirical restoration were easily removed using the scalpel. Next, a spray deacidification with BOOKEEPER was performed, and then the document was consolidated by applying a 35g/m² Japanese paper on the back of the document.

4. Conclusions

Along with the microclimatic and biological factors, the social factors affect the old documents, whose effects are often irreversible. The document investigated in the present paper, with a great historical and documentary value, witness of a controversial period in the history of the Romanian Countries, raised particular problems to the specialized restorer because of an empirical intervention performed at the beginning of the 20th century. The document

showed numerous ruptures, embitterment embrittlement and stains, both on the paper support and on the attached cardboard.

The scientific investigations aimed at identifying the empirical restoration materials, the biological attack agents and measuring the pH values. Using the DRIFT technique, it was established that the adhesive used during the empirical restoration was a natural resin, the mastic, with greenish fluorescence in UV light.

The correct identification of this adhesive, very rare in the case of documents with paper support, allowed to find the most suitable preservation treatment.

It is fortunate that such empirical restorations are performed only accidentally nowadays. This is due to the good training of the people who work in museums, libraries, archives through university, master's degree and continuing training programs.

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