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CONSERVATION OF PAPER DOCUMENTS DAMAGED BY FOXING

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Abstract

Within foxings, the paper is weaker, more acidic, and more friable than outside of them. Foxings can appear because of iron oxidation or due to the influence of microorganisms. At present, the nature of foxings is still under discussion. The chemical composition and structure of foxings are insufficiently characterized. Moreover, these processes can vary depending on external conditions and the original composition of the paper. The main goal of researchers and restorers is to find methods for prevention and slowing of the paper damage and oxidative destruction. The solution of this problem will make possible to save unique artworks, rare old books and documents.

Keywords: foxing, paper damage, oxidative destruction, iron oxidation, microorganisms

1. Introduction

The term foxing generally refers to small, roundish spot stains of reddish or yellowish brown colour, generally of small dimensions, with sharp or irregular edges, found in paper or other fibre-based materials. This term only vaguely describes the size, shape and colour of certain stains, of which interpretation may depend on each viewer's subjectivity.

The nature of these spots is not fully elucidated, although early research on this phenomenon, called foxing dates from 1930. Beckwith realized that the occurrence of foxing is related to the presence of iron in the composition of paper [1]. According to him the presence of metals inside the paper comes from the use of the hollander's beater (introduced in the manufacturing process by the end of the 17th century). It is therefore possible that the appearance of foxing to be caused by chemical reactions of iron traces from the paper (iron oxide and iron hydroxide) and organic acids produced by fungus. Hey concurred with Beckwith and proposed these dual mechanisms:

1. damp → mold acid → activation of iron → increased acid → mold death;
2. damp → activation of iron → increased acidity → local encouragement of mold → increased acidity → death of mold [2].

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Presence of foxing called 'Hoshi' (Star) on old Japanese papers, at which manufacturing were used traditional methods different from western ones, lead to the conclusion that iron is not the only cause for this phenomenon.

Another version linked by the emergence of foxing is that this would be the effect of microbial attack. In 1984 Hideo Arai managed, using scanning electron microscopy, to isolate and identify in the areas that had foxing, *Aspergillus glaucus* and *Aspergillus restrictus* which, he argued, would have caused the foxing on that support [3]. In 2000, the same researcher reproduced in the laboratory the same degradation phenomenon succeeding to identify the foxing mechanism [4]. However, there are researchers who believe that the experiment by Arai laboratory conditions do not accurately reproduce the appearance of foxing on the documents there are in libraries and book stores, so you can't say that his research are sufficient to explain this phenomenon.

Another observation regarding the volumes in libraries is that the microbial attack is located on the surface of the fore edge while inside is present the foxing. Also the humidity that is needed for the emergence of foxing is lower than the one that is needed for the visible mold [5, 6].

None of the two views on the occurrence of foxing can explain the phenomenon of foxing luminescence, although some microbiologists considered the luminescence as evidence of biological origin of foxing.

The microscopic, mycological and FTIR analyses of different stains on paper samples of different composition confirm that there is no relationship between the fluorescence under UV light and the vitality of fungal strains on paper [7].

Analysis of foxing by infrared spectroscopy has shown the presence of compounds containing carbonyl groups, unsaturated compounds with double bonds =C, =N, C=O, diene type ones with conjugated double bonds X=C=Y (where X is C or N and Y is C, N or O) bound with sugars. All mentioned compounds can be formed during the process of cellulose oxidation. Besides, they can be formed as a result of condensation reactions in the act of interaction of products of cellulose oxidation with nitrogen-containing compounds. The products of cellulose oxidation impart a peculiar colour to the stains, yellow for the double bond compounds, and brown for those containing nitrogen.

It was found that there is a direct relationship between the occurrence of foxing and the following aspects:

- **manufacturing mode of the support paper** of these documents (foxing paper is mainly produced between the end of the eighteenth century and beginning of the twentieth century; research conducted to date have shown that papers with a high content of lignin tend to undergo quick oxidative degradation processes, but are not conducive to the development of foxing [8]. Using the bleaching agents, of various additives have an important role in the paper's susceptibility to develop the foxing phenomenon.
- **The exposing time to light of the paper**. Foxing spots begin to develop on the edges of books, on parts of single sheets that are projecting from the book block or from a pile of paper, on the upper sheets of such a pile and on

cardboard bookbinding. They also tend to appear on drawings, engravings, single sheets of books, manuscripts and objects of cotton materials that were exposed for a long time.

- **dust laden of the environment in which it was stored document**. Foxing stains are located mostly on the front and back fly leaves, on margins of leafs, on the edges of books, in deformed parts of book blocks, on the illustrated pages. Such appearance is consistent with ways of penetration of dust into the book block. Obviously, these parts of the book block are subjects to the most profound oxidative damage. Sometimes we observed the formation of foxing in books and museum textiles on sections that were polluted in the process of use. There are also cases, when in process of conservation treatment of cotton fabrics, water polluted by iron compounds was used and this factor provoked foxing formation.
- **microclimatic parameters** (relative humidity, temperature). Research indicates that the internal moisture content of the paper must be at least 10% for fungal growth to occur. At 80% RH, paper in general absorbs 9-14% water, with more hygroscopic paper, a lower RH will permit mold growth. Iron alone will not corrode below 70% RH but in the presence of ions such as chloride, papers must be stored at 40% RH or lower to avoid iron corrosion [9].

As a summary of the above we can conclude that the foxing appearance may be caused by:

- metal directly oxidizing produces distinct dark centre and the migration of the soluble degradation products from the metallic centre causes the surrounding discoloration;
- microorganism contamination is mostly airborne in origin and produces irregular yellow-brown patches;
- metals and fungi produce acid in the cellulose which causes deleterious effect on papers;
- relative humidity increases the chemical reactivity of auto-oxidation, causing cellulosic discolouration in the wet/dry interface at the paper's surface.

2. Foxing classification

Cain and Miller have developed a classification of foxing types by shape, colour and UV fluorescence examination [9].

2.1. Bullseye

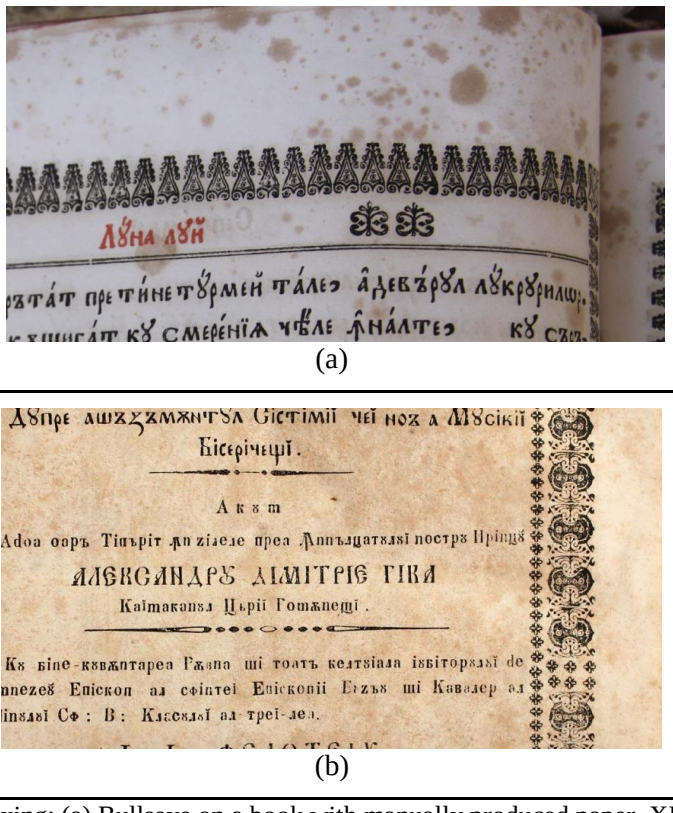
These spots are small and round, with a dark centre and concentric rings (Figure 1a). Bullseye foxing can be further subdivided by UV examination:

- Centres do not fluoresce (appear dark blue/black), rings fluoresce yellow/orange and pale yellow;
- Centres and rings do not fluoresce (appear dark blue/black).

This type of foxing always has metal cores, which do not fluoresce and appear dark blue/black.

2.2. Snowflake

These are spots with scalloped edges and/or irregular shapes which can measure inches across (Figure 1b). They are red/brown to yellow in colour but sometimes are not visible in normal light. It is theorized that the advanced stage of foxing causes coloration while the younger or dormant stage may not be visible in normal light. These spots appear to occur in association with fungal activity.



(a)

(b)

Figure 1. Foxing: (a) Bullseye on a book with manually produced paper, XIXth century, monastery deposit from Moldova; (b) Snowflake on a book with industrial produced paper, XIXth century, monastery deposit from Moldova.

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3. Identification methods

From the above lines appears the complexity of this damage called foxing. It can be said with certainty that even in the case of documents presenting foxing, developing a correct conservation treatment can't be made but only taking into account the principle 'no diseases but sick persons' and this can be

done only through a series scientific investigation. The literature presents several techniques to investigate the foxing documents: visual examination in normal light, transmitted light, microscopic examination, ultra-violet fluorescence (360 nm), spot tests (fungal activity, acidity, sampling of bullseye to perform iron test (potassium ferrocyanide, potassium sulphocyanide, potassium thiocyanate).

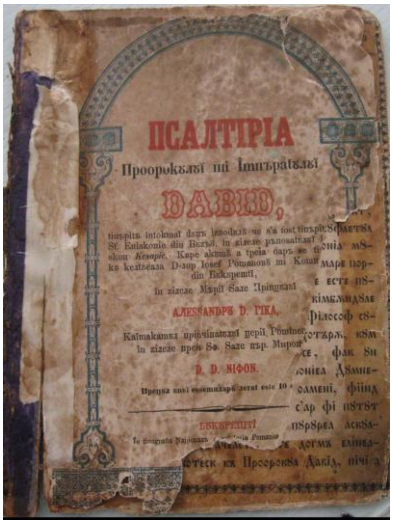
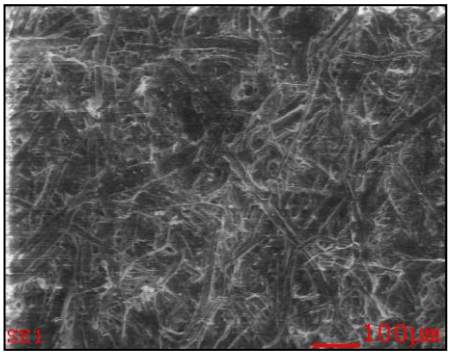


Figure 2. The book before restoration.



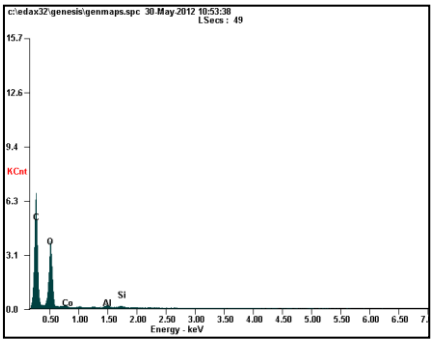


Figure 3. SEM-EDAX analysis.

4. Available treatments for foxing

- ***Environmental conditions monitoring*** **(**relative humidity, temperature, ventilation);
- ***Disinfection treatment*** of books and archival documents;

- ***Aqueous washing*** reduced soluble metal components, fungal bodies, their metabolites, and other impurities in the paper;
- ***Alkaline washing*** can cause those insoluble in water to become soluble in alkaline solution;
- ***Bleaching*** converting a conjugated double bond to a carbon-carbon single bond which removes discoloration from paper (hydrogen peroxide, sodium borohydride);
- ***Aqueous light bleaching*** decrease discoloration immediately for both sized and unsized papers;
- ***Metal removal or inactivation*** – mechanical or chemical – with sodium dithionite, chelating agents (EDTA, oxalic acid), alkaline treatment of metal ions.

5. Case study

The book was printed in 1856 in Bucharest, and comes from a monastery book store in northern Moldavia (Figure 2). The paper presents complex physical degradation, chemical, biological, social, evidenced by waving, tears, embrittlement, cracking, fracture, lacks support, and yellowing caused by aging, foxing, colour changes caused by biotic attack.

Since the foxing phenomenon is frequent on the paper in the analysed book, it required special attention. The SEM-EDAX analysis (Figure 3) excluded the presence of iron in areas showing foxing, being identified only traces of cobalt and aluminium). However, biological investigations confirmed fungal paper attack (*Trichoderma viride*, *Penicillium sp.*, *Aspergillus niger*, and *Chaetomium sp.*).

The restoration and conservation treatments (Figure 4) which were approved by the Commission of Restoration and made in our laboratory consisted in: disinfection treatments (with 40% formaldehyde in oven), dry cleaning, dismantling the book block, cleaning with solvents, attenuation of foxing stains by local dabbing with a hydrogen peroxide solution, followed by wet cleaning treatment and aqueous deacidification with a solution of $Ca(OH)_2$.

Consolidation operations and reunification of paper support was done with Japanese paper ($11g/m^2$ and $18g/m^2$ with the weights) and CMC solution (2%). Finally was restored the book block.

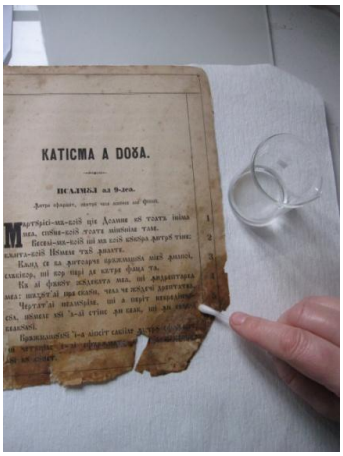
In the added documentation were also mentioned the conditions which must be provided the owner of the book (salubrious area with microclimatic parameters: 50-55% RH, T 1-18 ° C).

6. Conclusions

Foxing stains are a common problem in cellulosic heritage materials conservation and, despite decades of research, their cause is still not understood. Some authors found evidence of bacterial or fungal growth in some foxed areas sometimes associated with the presence of iron. Analytical techniques available

for investigation are described, sources of paper decay are listed and methods for treatment also suggested.

(a)



(b)

(c)

(d)

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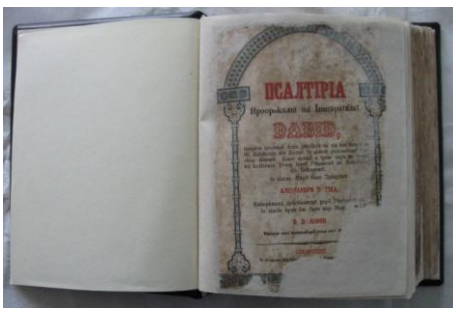

(f)

Figure 4. Aspects of the conservation-restoration treatments: (a) dry cleaning, (b) cleaning with solvents, (c) wet cleaning, (d) aqueous deacidification, (e) removal of the excess of Japanese paper used for completion of lacking zones, (f) the book at the end of conservation-restoration treatments.

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