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Ethylene Oxide for Book Fumigation

Abstract

The contribution reports on the EU project “Men and Books”, which deals with written heritage of the Archives of the Protestant Parish of the Holy Trinity in Świdnica. This archive is one of the most valuable repositories for the history of Protestantism in Silesia, Bohemia, Moravia and Austria. Due to uncontrolled climate conditions in the past, many of the books were attacked by microorganisms. During the 1990s and in the years 2009 and 2010 the books of Świdnica were fumigated with ethylene oxide. The use of ethylene oxide for book-disinfection is considered highly controversial in the prevailing literature and whether or not ethylene oxide is a valid choice for book-fumigation still remains an open question. The question put forward is whether or not ethylene oxide harms material and/or the readers and if the fungi is killed.

So far no off-gassing Ethylene oxide could be detected. GC was used. The original infestation with microorganism was killed, but new infestation exists.

1 Introduction

Book and paper conservators and archivists all over Europe are fighting the intractable problem of moulds. Moulds destroy our cultural heritage. This is especially true for books and charters in archives. These resources, being unique in their nature, and thus, extremely valuable for the understanding of Europe’s past, are at risk of being lost due to the effects of microorganisms. This destruction occurs for a multitude

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of reasons. Primarily, there exist fungi that particularly attack and destroy paper and parchment. Secondly, archival material is stored in big compact bodies and is comparatively rarely moved; therefore, infestation often stays undiscovered for a long time until it is so vast that it cannot be overlooked.

Mouldy material is a serious health hazard for both archivists and readers, as most of the spores cause dangerous illnesses. Furthermore, current methods of disinfection are conducted using an array of toxins.

The EU project, “Men and Books – for a risk-free use of the European written cultural heritage”, seeks to find a solution for extermination of the mould with a substance and a method, that would be harmless for both humans and books. This would be beneficial for all European users of archival material.

This contribution deals with the measurement of off-gassing of ethylene oxide and seeks to estimate the toxicity and the impact that the ethylene oxide treatment has on the collagen material such as leather and parchment.

2 Description of the Archival Material – Putting forward the Question and stating of the problem

The EU project “Men and Books” deals with bound volumes of the Archives of the Protestant Parish of the Holy Trinity in Świdnica, where 12,000 individual items are stored. This archive is one of the most valuable repositories for the history of Protestantism in Silesia, Bohemia, Moravia and Austria. Due to uncontrolled climate conditions in the past, many of the books were attacked by microorganisms – mainly fungi. During the 1990s as well as in 2009 and 2010 the books of Świdnica were fumigated with ethylene oxide. The use of ethylene oxide for book-disinfection is considered highly controversial¹ in the

1 Standards EN 1422 and EN 550 allow for the use of ethylene oxide for sterilization of certain medicine materials. A German law dating back to 1981 forbade using ethylene oxide for fumigating food. For books, no regulations exist. For more detail please see also Meier/Petersen (2006) and Sterflinger/Pinzari (2011).

prevailing literature and whether or not ethylene oxide is a valid choice for book-fumigation still remains an open question.

Without a doubt, fungi in archives are dangerous for both those who work there and for the books². However, some of the methods for disinfection are hazardous for both books and humans. Therefore, it was the aim of the study in this EU project (a) to analyze if there was an active fungal community on the ethylene oxide-treated books or if the treatment was effective³, and (b) to investigate possible remains of ethylene oxide that might not only still have an impact on the microbial community and protect the books against microbial attack, but also might be health-threatening for the reader of those volumes.

For the project there were 76 books selected, 44 manuscripts and 32 prints. They represent an essential corpus in terms of their information value and in the possibility to transfer research results to any other library or archive in Europe.

3 Description of the Task

The tasks of the entire research project were distributed to the partners. The obligations described in this contribution were defined as follows:

- measure off-gassing of ethylene oxide
- evaluate levels of toxicity (this task was subcontracted to Environment Agency Austria (Umweltbundesamt)
- provide test samples
- analyze parchment and leather
- interpret – analyse results
- develop guidelines for the restoration
- develop recommendations for the handling of mould-attacked heritage archival material and handling of ethylene oxide-fumigated heritage archival material on paper, parchment and leather

2 Samson et al. (1994)

3 This topic will be dealt with by Katja Sterflinger, University of Natural Resources and Life Sciences, Muthgasse 18, 1190 Vienna

- suggest alternative methods to disinfect mould-attacked written/printed heritage objects
- disseminate the project results in numerous ways (via a website, in journals, by organizing a conference and an exhibition, by teaching ERASMUS students, etc.).

In this contribution, the focus lays on the effects of ethylene oxide treatment on books in terms of its effects on both humans and the archival material.

3.1 Measuring the off-gassing of ethylene oxide

28 books were selected for measuring the potential off-gassing. For the selection of books, several parameters were relevant:

1. moment of ethylene oxide fumigation (17 books were fumigated in 2009, 11 were fumigated in 2010)
2. material composition (11 printed books, 7 manuscripts written in iron gall ink, 10 modern manuscripts written in dye ink, 15 books had leather in their binding, 3 books were bound in parchment, 11 books were bound in textile; all books were of contemporary paper)
3. age of the books (2 books were from the 18th century, 12 books were from the 19th century, the rest were from the 20th century).
4. size of the books (folio to octavo).

These parameters represent an average in terms of the above features found in European libraries and archives. This is especially important when it comes to transferring the results of the project for application Europe-wide and on an “average archive” at the end of the project. 28 volumes bound in leather, parchment, paper and textiles, dating from the 18th, 19th and 20th century also represent different sorts of paper as book block.

The books were selected by the Świdnica parish and brought to the European Research Centre for Book and Paper Conservation-Restoration in Horn. The books were put into a 1 m³ chamber of inert synthetic

material and stored under closed conditions for 60 days at 20 °C and 50% RH.

In order to fully understand the resulting data, we search for more information on the fumigations which these books had previously undergone was made. The following information⁴ was found:

- A fumigation had been executed from April to August 1994
- 346.2 running metres of books in total (261.2 m, 85 m in folders, 13 m notes) were treated. The following measures were taken then:
 - Sources of damage were analysed. The results were the following: The books were stored in wet/very humid conditions. The books were dusty and there were spores in the dust, posing a risk for human health. 10 years before (i. e. in 1984) the books had been brought to dry rooms, but, due to tight packing, failed to dry up sufficiently fast.
 - Both humidity and temperature were measured in 50 books in July 1994, with the RH being between 59% and 71% and the temperature between 19.5 °C and 23.4 °C. The humidity of the air in the room was between 57% and 62% RH and the temperature was at 22.6 °C.
- 9 books and 15 groups of archival documents were selected according to various criteria (type of damage, material composition, content) and subjected to a model conservation treatment⁵.
- Microorganisms were analyzed by microscope observation directly on the books or, in complicated cases⁶, on a growth medium. The following species of fungi were found: *Streptomyces*, *Geotrichum*, *Chaetomium*, *Acremoniella*, *Stachybotrys*, *Epicoccum*, *Stemphylium*, *Botrytis*⁷.

4 The following information is a translation from a letter by our partner in Świdnica after a report from November 1994. The text is not fully understandable in some details, however, the author had no possibility to clarify those details. Still, even though some details are not fully clear, the text provides valuable information.

5 The author understands the term “model conservation treatment” as being a conservation treatment which has the impact to serve as a good example.

6 The author does not know what the author of the report means with “complicated case”.

7 *Streptomyces* are bacteria, the other are fungi. The author would like to thank Flavia Pincari for this comment.

- The entire collection plus the 9 books and 15 groups of archival material mentioned above were packed and prepared for disinfection
- Fumigation with 90% EtO and 10% CO₂ (Petrox gas) was executed
 - A 20 m³ chamber was used, 10 kg Petrox⁸ were applied, the treatment lasted for 5 days, then air-washing was performed until EtO detectors⁹ did not show EtO any more.
 - The rooms of the archive were disinfected with 2% Aseptin M¹⁰ solution. The treatment was repeated after 10 days.
- Books were air washed and acclimatized.¹¹

Furthermore the quoted text reports:

- In Świdnica dust and microorganism spores were removed from the books in September 1994 (after the report was written [remark by the author]).
- The effectiveness of the disinfection was evaluated.¹²

In 2009 and 2010, another ethylene oxide fumigation had been conducted. Concerning data of the fumigation, the Ossolineum in Wrocław¹³ (Konvak s.c.) gave the following report: “The books were fumigated according to a standard operation procedure, which is a 24 hours fumigation with 9% ethylene oxide followed by 15 times air washing. The chamber holds 500 litres. After this treatment, the books were put into separate storage for another 7 days.”¹⁴ Further details were provided by

8 According to the information from Poland this is 90% EtO and 10% CO₂

9 We are not able to define which kind of detector was used or give a reference on the type of measurement used. The report reached us as we quote it here.

10 It is a ethyl 4-hydroxybenzoate or 4-hydroxybenzoic acid ethyl ester, with CAS Number: 120-47-8. This compound falls in the “Paraben” group. 4-hydroxybenzoic acid ethyl ester (thanks to Flavia Pincari for her help in understanding the composition of Aseptin M.

11 T° and UR% are not known

12 We do not know how this was done and we have no possibility to find it out.

13 Letter by Mariusz Jaskulski, Zakład Narodowy im. Ossolinskich from 6th March 2013.

14 Letter by Sonja Stankowski was translated from German by the author.

Adam Wilga¹⁵: “The chamber used in the process holds some 5 m³, the gas is so called “S-9”, a mixture of 9% EtO and 91% carbon dioxide. At the start of the fumigation the pressure is lowered to 2 bar and the temperature is elevated to *c.* 30 °C. The gas is inserted in a shielded way, so that it is not directly pumped onto the books. During the fumigation the temperature is 25 °C, the RH 50% and the pressure 850 mbar. The chamber of stainless steel is filled for 30 minutes. After treatment, the books are immediately brought to a chamber for air washing. There they stay for 3–4 days under atmospheric pressure. The air is sucked off through a HEPA filter. To extract the leftover gas from the books, the pressure is put up to 50 mbar for 15 minutes, and the air washing is performed under 500 mbar. This is repeated 15–17 times.¹⁶ The safety data sheet also provided references to EG law Nr. 1907/2006 (REACH) and 453/2010.¹⁷ The gas itself was attested by Nr. 03723.¹⁸

In 2012, one of the questions of the EU project was whether or not there still was any EtO gassing off the treated books of Świdnica. Two different analytical methods to detect the the potential offgassing of ethylene oxide were chosen: (a) measurement with a Dräger X-am 5000 digital handheld device which turned out to be too approximate (measuring range 0–200 ppm, resolution 0.5 ppm, smallest possible detection 1 ppm, which was above the expected concentration) and (b) a Gas Chromatography/Flame Ionization Detector. The latter method was a passive measurement with ORSA-tubes filled with activated carbon. The measurement lasted for 336 hours. Then the tubes were taken out, closed, and sent for gas chromatography.

The detection of the EtO was performed by means of a solid sorbent collection, derivatization and gas chromatography measurement. The EtO adsorbed on the carrier columns was performed by means of a gas

15 Communication via Sonja Stankowski who was translating the Polish reports into German, Affiliation of Adam Wilga was not given.

16 Mail by Sonja Stankowski from 13th May 2013.

17 Same mail different attachment.

18 09-402 Plock 4, Skrytka pocztowa 66, ul. Długa 3, Poland; EtO content 99.9%, water 0.0087%, aldehydes 0.0069%, acids 0.0010%, CO₂ 0.0010%, not volatile components 0.0031%, Platinum cobalt color number: 5. Source: 3rd attachment, same mail.

chromatograph interfaced with a flame ionization detector (FID) following a method developed by the National Institute for Occupational Safety and Health (NIOSH Germany). Two columns were used (30 m OPTIMA-WAX; 0.53 mm × 1.0 µm and 30 m OPTIMA 1; 0.53 mm), with Nitrogen as carrier gas, and artificial Air and Hydrogen as burning gases (Nitrogen: 2.5 mL/min. Synth. air: 300 mL/min, Hydrogen: 25 mL/min. Stove temperature 45 °C isotherm 10 min, 45 °C to 180 °C in 5 °C/min; 180 °C isotherm 13 min, 180 °C to 200 °C in 10 °C/min, 200 °C isotherm 13 min).¹⁹

No ethylene oxide was detected.

3.2 *Evaluation of toxicity*

The report by Environment Agency Austria (Umweltbundesamt), Vienna, a subcontractor of the European Research Centre for Book and Paper Conservation-Restoration in this project, and an expert on the questions involving toxicity to humans, focused on the health risk EtO-fumigated books might pose for the reader and the archivist. The report stresses that books fumigated with EtO may also emit EtO reaction products including ethylene chlorohydrin (ECH) and ethylene glycol (EG), the latter substances also known to be detrimental to human health, which were not taken into account in the project.

The maximum exposure level, for which the cancer risk is considered of very low concern, derived from this report, is 0.02 mg/m³ ethylene oxide and is in line with the assessment of AGS²⁰ (2011).

Provided that the study results are valid, the ratios of risk posed by using the treated books indicate that the risk is acceptable for non-cancer effects and of very low concern for cancer effects. However, the

19 NIOSH Manual of Analytical Methods, 3rd ed., Vol. 1, Method 1614, Department of Health and Human Services (NIOSH) Publ. No. 84-100 (1984). I would like to thank Dräger Analysenservice for performing the analysis. A "Doppelsäulengerät Sichromat 1-4" was used to make analysis.

20 "Arbeitsplatzgrenzwerte", a value allowed at working place

study was assigned a Klimisch score of 3²¹. It has to be taken into account that the books used for the first test series could only demonstrate the potential EtO offgassing from a limited quantity of material. The concentration of EtO in air can increase considerably depending on the number of books stored within a closed room or cupboard. It may be necessary that the EtO concentration in air is monitored in such storage rooms. If it cannot be assured that the concentration in the air is below the safe limit, risk mitigation measures have to be applied, such as, for example, sufficient technical ventilation.

It was recommended by Environment Agency Austria that those responsible for the fumigation process, follow the guidance TRGS-513²², which considers as acceptable the concentration of EtO in air of 0.02 mg/m³ instead of 0.2 mg/m³.

3.3 Making test samples

In order to understand the effects that EtO might have on the material, test samples had to be made. On the one hand, the dummy material had to represent the original material as closely as possible. On the other hand, it had to have a limited number of parameters, which would enable the researchers to make meaningful interpretation of the results.

Whatman I filter paper, as this is a well-known standard in conservation research was used as well as parchment by Wildbret²³ and sumach-tanned leather produced by Forschungsinstitut für Leder und Kunststoffbahnen²⁴.

21 "This includes studies of data from the literature/reports in which there are interferences between the measuring system and the test substance or in which organisms/test systems were used which are not relevant in relation to the exposure (e.g., unphysiologic pathways of application) or which were carried out or generated according to a method which is not acceptable, the documentation of which is not sufficient for an assessment and which is not convincing for an expert judgment."

22 Technische Regel für Gefahrstoffe 513 – www.baua.de/de/Themen-von-A-Z/Gefahrstoffe/TRGS/TRGS-513.html [13th Oct. 2013]

23 Calf parchment, Wildbrett, Waldstrasse 20, 86399 Boblingen BRD

24 Product Nr. A 001936 calf 09599 Freiberg Meißner Ring 1–5, BRD

The material was divided into 24 portions:

- A, B and C were the short names for paper, parchment and leather, while numbers from 1 to 8 stood for the treatments:
 - no. 1 went straight to EtO fumigation and then surveyed,
 - no. 2 went directly for mould infestation and then surveyed,
 - no. 3 was infested with mould and then treated with EtO and then surveyed,
 - no. 4 was only made and stayed untreated as reference material,
 - no. 5 was aged artificially after it was made and stayed as reference material for aged paper, parchment and leather,
 - no. 6 was aged and then EtO fumigated,
 - no. 7 was aged, infested with mould and surveyed, and
 - no. 8 was aged, infested with mould and EtO fumigated and then surveyed.

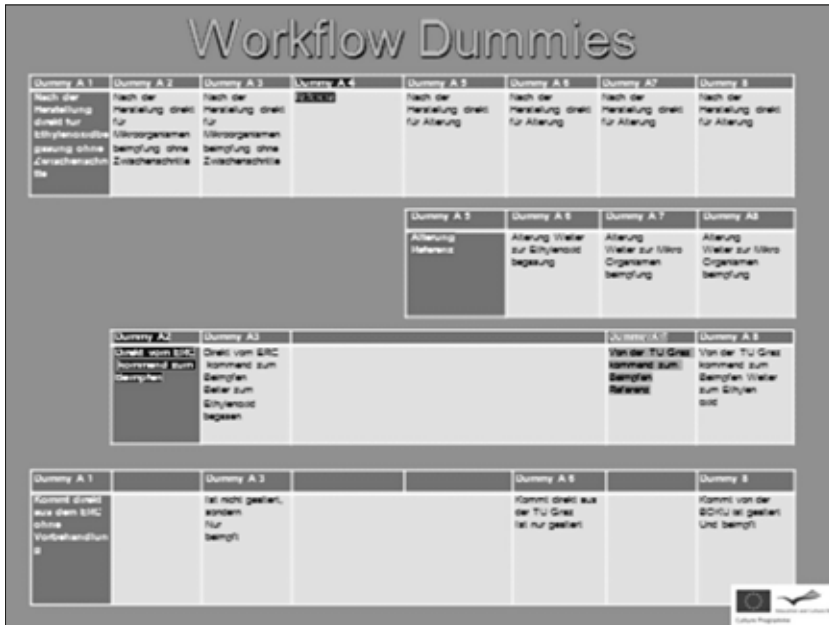


Fig. 1 Work flow of dummy preparation

Artificial ageing was performed after ÖNORM Regel – ON 1116 procedure at the Technical University Graz, a project partner and mould

infestation was done at the University of Natural Resources and Life Sciences Vienna, another partner in the project. For the paper, 300 cycles of humidity-temperature fluctuation gave a good result. For parchment and leather this ageing is not a standard, however, 250 cycles were applied.

The mould infestation data, together with the respective results on the microbiological aspects of the research, are published elsewhere.

3.4 Analysis of the parchment and leather test samples and interpretation of results

The parchment samples and leather samples were surveyed for fibre length after Larsen and shrinkage temperature²⁵ was measured. The reference parchment had Larsen 2 fibre length and a shrinkage temperature of 50 °C. We could not detect other intervals. The leather had a fibre length of 1 after Larsen and shrinkage intervals of A1: 52.2; B1: 65.3; C: 74.0; B2: 79.1; A2: 85.9 (average of 20 measurements)²⁶.

The aged test samples had become gelatinized due to the elevation of RH during incubation (for 4 weeks light room temperature and c. 90% RH) and thus especially the infested test samples could not be surveyed according to the standards.

As soon as the uninfested material will be back from the EtO fumigation it will be possible to compare the leather and parchment before and after fumigation. These results will be published later.

25 Larsen et al. (2002)

26 The author thanks her students Shirin Jacoby, Bogna Górnica, Marta Cieplinska and Marta Swieton, Nikolaus Kopernikus University, Torun, Cristina Cicero from University of Rome II, "Tor Vergata", Rome for making the measurements.

3.5 *Development of guidelines for the restoration*

As the project will be concluded only in a few months' time, this task will also be finalized only then and the results will be published later.

4 Next steps

As no ethylene oxide was detected with the methods used so far, the author decided to include another test into the project, i.e. going beyond the original work plan. Some books were prepared to be freshly fumigated together with the test samples which had to undergo fumigation within the framework of the project. This way, as the test samples obviously had too little volume to hold a measurable amount of EtO, a larger quantity of material was prepared for ethylene oxide fumigation and the chances of detecting off gassing EtO and getting more meaningful numbers allowing extrapolation to the entire archive stock, were increased.

A second advantage of fumigating additional books would have been that it would have certainly given a chance to control and monitor precisely the conditions to which the books are exposed during and after fumigation. In contrast to the vague information provided concerning the previous fumigations, these precise data, together with the results of a second gas chromatography measurement, could contribute in a larger measure to proper interpretation of the data on human toxicity.

A PTFE – glass sheet²⁷ was bought and sent to the fumigation specialist. He was asked to wrap the books immediately after fumigation would be completed. The data of the foliar are: basis material: glass embedded in Polytetrafluorethylene, 60% ± of the entire material, thickness: 0.128 mm, weight: 272 ± 5% g/m². The fumigation had to be monitored accurately and the wrapping of the books after fumigation had to be documented thoroughly, too. Unfortunately, the tests were still ongoing when this contribution had to be handed in, and the final results will be published later.

²⁷ Provider Hans Reiter, Ecosolution, Bahnhofstr. 100, 8401 Kalsdorf bei Graz

Furthermore the report of Environment Agency Austria (Bundesumweltamt) stressed that books fumigated with EtO may also emit EtO reaction products such as ethylene chlorohydrin (ECH) and ethylene glycol (EG), the also known to be detrimental to human health. Another project will be submitted, focusing on these products of EtO.

5 Conclusion

This project has shown so far that the methods applied in the project do not detect any presence of EtO in properly air-washed books and archival material. We have information from the partner University of Natural Resources and Life Sciences, which allows us to estimate that EtO did kill the mould which had been on the books before the treatment. Side products of both fumigated moulds and EtO reaction products concerning its toxicity to man, i.e. readers, must still be surveyed. Further tests are ongoing.

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