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OLD CONSERVATION MATERIALS AND METHODS ON PARCHMENT DOCUMENTS

Zusammenfassung

Materialinhärente Information wird immer stärker durch Philologen genutzt. Restaurierungsmittel- und –methoden verändern das Material von Handschriften etc., in der Absicht es zu stabilisieren und das Fortbestehen der Originale zu sichern. Hoch an der Zeit ist eine Untersuchung, ob und wie die im Material enthaltenen Informationen durch Restaurierungen verunklärt oder sogar unlesbar gemacht werden. Der Beitrag nimmt diese Frage an Hand von Pergamentuntersuchungen mittels Restaurierungsverfahren von O. Wächter und modernsten MALDI TOF Untersuchungen im Zuge einer interdisziplinären Forschung in Angriff.

Keywords: old conservation methods, parchment conservation, information kept in the material

Introduction

The impact of conservation methods on cultural heritage items is a topic that has recently been understood as important and, therefore, was suggested as a new research area at the American Institute of Conservation (AIC) meeting[1] in Houston in 2018. For the particular field of paper conservation, a survey of what was considered the most relevant literature of the past years has been published by Zervos.[2]

However, the publication only covers a part of its intended field. It avoids any mention of changes in philosophical and theoretical approaches of the profession[3] and does not attempt a survey of the cultural heritage item in its entirety,[4] because Zervos only focuses on paper as a carrier of text. The author will present a new survey taking the conservator's perspective at the MATCONS 8–12 Oct. 2019.[5]

Another shortcoming of the research thus far is that the obviously outdated

1 https://www.culturalheritage.org/events/annual-meeting (June 2018)

2 S. Zervos, I. Alexopoulou, I. (2015), 'Paper conservation methods: a literature review', in: *Cellulose*, 22 (5), 2859-2897.

3 An overview is provided in: H. Riedl, P. Engel, 'Systems, patterns and fractals – Both decay and conservation in the Sisyphusposition', in: *ERC Newsletter*, 2/2015, pp. 18-25, most important U. Schädler Saub, D. Jakobs, *ICOMOS Hefte Deutschland X*.

4 P. Engel, 'Books Convey not only Knowledge, but also Beauty', http://www.icininfo.net/index.php?option=com_content&view=article&id=55&Itemid=59

5 P. Engel: 'Comprehensive criticism of conservation methods – their capacity to alter the material the documents, drawings and books are made of at MATCONS 2019'; https://www.muzeulolteniei.ro/en/api/article/view/id/cultural-agenda-c256

methods on conservation only rarely become a topic of research. The application of old methods, in contrast, has been altering the information conveyed by the very material of manuscripts over many decades; therefore, scholars, such as philologists who increasingly include the information carried by the material itself into their research, get misleading information.[6]

Finally, literature in languages other than English is hardly recognized at all in recent research in this field, although these instructions about how to preserve documents have influenced conservation activity over many decades and continue to do so.[7]

The team of the European Research Centre for Book and Paper Conservation-Restoration, therefore, strives to intensify the research into the topic of "fingerprints" of old and outdated conservation methods and the history of book and document conservation.

This contribution aims to be one piece in the whole mosaic and clarify the possible impact of old conservation methods on leather and parchment conservation results, using recipes brought together by Otto Wächter,[8] one of the pioneers in graphic art and book conservation, whose ideas have been taken up Europe-wide. A better study of his ideas, suggestions, and methods would clearly benefit the understanding of conservation-related findings in a large number of collections throughout Europe.[9]

Method

To demonstrate the above, the team of authors started out with the analysis of Otto Wächter's "*Restaurierung und Erhaltung von Büchern, Archivalien und Graphiken*", from 1982. The choice of the book was determined by two considerations: first, it was highly influential in its time, as said above; second, it is difficult to interpret if you were not a pupil of Wächter, and Engel was his pupil.

Wächter provides the recipes in a summary style, which makes it necessary to recall practical work with Wächter in the 1970s and 1980s in order to remember what was actually meant with the texts. In many cases, no concentrations are given for solutions and no description of how to apply a substance nor how long to let a substance react with, for example, a stain on the parchment is given.

As a first step, all the materials had to be brought together or had to be prepared.

There are several materials that are not available anymore, of which natural sperm oil is the most significant for our research. Hunting sperm whales is now prohibited and, therefore, fresh natural sperm oil can no longer be procured.

In some cases, the application could be simulated without recreating the damage that should be treated with the individual substance and method; in other cases, the re-creation of the problem had to be the first step, and the application of the conservation method was the second step. The decision as to whether or not the damage had to be recreated was based upon the question whether or not a research question, such as, "Did the conservation method and material alter the parchment in its internal information?", could be answered without the re-creation or only by re-creating the damage. The latter was the case, for example, when the period of the reaction of the substance with the parchment was dictated by the success of the result.

Both the conservation material and method and the re-creation of damage have been documented.[10]

6 Projects by Prof. H. Miklas University Vienna would be examples https://cima.or.at/heinz-miklas/ (19th July 2019)

7 O. Wächter, Schweidler, W. Wächter, Trobas would be important sources in the German language.

8 O. Wächter, *Restaurierung und Erhaltung von Büchern, Archivalien und Graphiken,* (Graz: Böhlau, 1982).

9 The contribution became possible due to the fact that Engel was invited to cooperate with Prof. Matthew Collins and his team, who recently won an ERC advanced grant https://sites.google.com/palaeome.org/ercb2c/home

10 Please see Table 1 for details.

Table 1: Table of recipes

Running Number	Sample preparation	Recipe as it was executed on the samples	The purpose	Observations	Hypothesis
1	An iron gall ink made after the recipe by Boltz von Ruffach* was applied to the parchment on both sides with a stick at around 18 °C room temperature and then the ink dried naturally.	**Sodium hydrogen carbonate solution** (10% in water) was applied onto the ink line with a glass pipette. Barium hydroxide was not used as I was not able to obtain it at a reasonable price.	Preventing ink corrosion.		Water might lower the shrinkage temperature.
2		Parchment A was rubbed with eraser powder a **Factis mix** (still old material from the 1980s, "Archival Aids Draft Clean Powder DCP32lb" by Ademco Limited) in a gentle way on both sides and then the powder was brushed off as we did in those days.	Dry cleaning.		Factis crumbs will stay in the parchment structure by electrostatic forces and age slowly, giving the parchment an overall yellowish hue.
3		**Water/70% ethanol 1:1 Vol %** was mixed at room temperature. The parchment was immersed and massaged for 2 minutes with a brush. Then parchment A was taken out and placed on oil paper,** and weights were placed along the margins of the piece.	Wet cleaning.		The shrinkage temperature will be lowered.
4	Parchment A was artificially aged for 60 days at a fluctuating temperature between 18 and 35 °C and a fluctuating humidity between 55 and 10 % rel Hum. Altering every 12 hours.	**Humidification chamber**: cold water mist was produced by natural evaporation of water from a basin for 2 hours, aged parchment was placed over the bowl with cold tap water for 2 hours. Thereafter, light pressing.	Softening.		The shrinkage temperature will be lowered.
5	Parchment treated like recipe 4.	I applied **glycerine** with my hands.	Softening.		The shrinkage temperature will be lowered.
6	Old parchment glue with vinegar.	The glue was sent as a liquid, and **parchment glue** was applied to parchment A by brushing with a brush.	Softening.		Alteration of information concerning animal.
7	Preparation of parchment glue: leftovers of parchment (animal not specified) are cut into small pieces, cold water is added 3-4 times, and they are left to swell at least overnight (10 hours). Then cooked in water bath for 24 hours. Put cardboard strips between the 2 pots; the solution should not become hotter than 70°C; ideal temperature is 50°C. the water that evaporates must be substituted by new water constantly, sift through a cloth, add vinegar of 7% 1/3 of the amount of the glue, add 1/3 of the amount alcohol, shake.	**Parchment glue** was applied to parchment A with a brush.	Softening.		Alteration of information concerning animal.

* Valentin Boltz „Von Dinten", *Illuminierbuch. Wie man allerlei Farben bereiten, mischen und auftragen soll. Allen jungen angehenden Malern und Illuministen nützlich und förderlich*, 1549. Reprint with introduction and indices ed. by J. Benziger (Nendeln: Sändig, 1976).

** Oil paper was kindly given by the archives of the Technical University Vienna.

Running Number	Sample preparation	Recipe as it was executed on the samples	The purpose	Observations	Hypothesis
8a/b	Parchment A was touched with vegetable cooking-oil on two spots, one closer to the "A" mark and one further.	The stain closer to the mark was treated with **magnesia oxide** and the farther one with **sepiolite**. **Benzine** was mixed with MgO and sepiolite each separately and applied onto the stain from the top. The poultice was left to dry at room temperature. Then the poultice was removed with a dry brush. The measure was repeated twice, then the stain was gone.	Removing grease stain.		Residues of the powders that might alter the information of the original treatment of the parchment with inorganic powder (calcium carbonate, etc.) Information om the source of the powder might be irritated or made impossible.
9a/b	Parchment A was touched with vegetable cooking oil to create two stains.	For the **ether** application, the areas of the 2 stains were put onto sepiolite and MgO, and the ether was dripped onto the stain from the top.	Removing grease stain.		As 8/ab.
10a/b	Parchment A was touched with vegetable cooking oil to create two stains.	For the **chloroform** application, areas with the 2 stains were put onto sepiolite and MgO and the chloroform was dripped onto the stain from the top.	Removing grease stain.	The chloroform did not stay in the area where I applied it, but ran all over the parchment sample 10a/b.	As 8a/b.
11	My blood was applied onto a parchment B to both sides and dried for 7 days.	Half of the stain was made wet with tap water from one side and put upside down over the open bottle of 30% $\mathbf{H_2O_2}$ for one hour at around 18 °C.	Removing blood stain.		Lowering shrinkage temperature.
12	Ballpoint pen lines were put onto parchment.	**Dimethylformamide** was dripped onto the area and the lines were rubbed off with a cloth.	Removing ballpoint pen ink stain.		
13	Parchment aged.	Aged parchment A was immersed into **milk (supermarket 3.5% fat)** for 2 minutes massaged a bit and then air dried.	Softening.		Lowering shrinkage temperature, slight fat – tanning.
14	Parchment aged.	Aged parchment A was immersed into urea 10% for 2 minutes and then massaged a bit and then air-dried.	Softening	The parchment became really stiff and not at all soft.	Lowering shrinkage temperature.
15	Parchment was aged.	Aged parchment A was immersed into **cedar oil** for 2 minutes and then massaged a bit and then air-dried.	Softening.		Slight oil-tanning.
16		Parchment A was dipped into **dimethyl sulfoxide**.***	Removing stain.		
17		Parchment A was dipped into **ammonia**.	Removing stain.		

*** The authors thank Ralf Witting for helping with some of the solvents needed.

Running Number	Sample preparation	Recipe as it was executed on the samples	The purpose	Observations	Hypothesis
18		Parchment A was dipped into a solution of **soluble nylon (from the 1980s) in toluene** (supersaturated solution).	Nylon was used as protection of colours.		
19		Parchment A was placed over the opening of a bottle holding 5 ml 30% **H_2O_2** and 3 drops of **ammonia** for 30 minutes.	Removing stain.		
20	Wheat starch paste was prepared of 1 vol part wheat starch and 4 vol parts tap water, boiled for 2 minutes and cooled to room temperature.	**Paste** was brushed onto parchment A flesh side.	Mending tears.		Lowering shrinkage temperature.
21	As in 20, but after the paste was cool, **Nipagin** was added to the paste before it was applied.	**Paste with Nipagin** was brushed onto parchment A flesh side.	Mending tears.		Lowering shrinkage temperature.
22		Parchment A was dipped into 5% **oxal acid** for one minute, taken out and dried at room temperature without rubbing.	Removing rust stains.	The parchment curled up while drying.	Shrinking.
23		Parchment A was immersed into 3% **HCl** for one minute, taken out and dried at room temperature without rubbing.	Removing rust stains.		
24		Parchment A was immersed into **Titriplex** 10% in water for one minute, taken out and dried at room temperature without rubbing.	Removing rust stains.		
25		Parchment A was immersed into a mixture of **H_2O_2 : ether** 1:1 Vol parts for one minute, taken out and dried at room temperature without rubbing.	Removing fly excrement.		
26		Parchment A was immersed into warm 10% **Borax** solution for 5 minutes, taken out and dried at room temperature without rubbing.	Removing milk stains.	When the parchment was dry the crystals were like shiny snow in winter light on the surface of the parchment.	
27		**Nitroverdünnung** (nitro-thinner is a mix of organic solvents such as ketones, esters and alcohols) was dropped over parchment A 3 times on both sides and then the parchment dried at room temperature.	Removing synthetic adhesives.		

Running Number	Sample preparation	Recipe as it was executed on the samples	The purpose	Observations	Hypothesis
28		Parchment A was immersed into **acetone** for one minute, taken out and dried at room temperature without rubbing.	Removing synthetic adhesives.		
29		**Hot water and turpentine soap**, parchment A was massaged for one minute with turpentine soap foam made with a brush first dipped into hot tap water and then moved over the turpentine soap. After the treatment, the soap was washed off the parchment with warm water and the sample left to air dry at room temperature.	Cleaning off ink stains.		Lowering of shrinkage temperature.
30	Fish bladder was soaked in cold water overnight and warmed in a water bath the next day over several hours. The fish bladder was from an old source in the USSR.	A small brush was dipped into the isinglass, and the glue was brushed onto the parchment A, after this the sample was left to dry at room temperature.	All sorts of gluing, like mending tears, etc.		Change of information about animal and lowering shrinkage temperature.
31	Parchment leftovers were soaked in cold tap water for 2 days and then warmed in a water bath the next day over several hours.	A small brush was dipped into the glue, and the glue was brushed onto parchment A, then the sample was left drying at room temperature.	All sorts of gluing, like mending tears, etc.		Change of information about animal and lowering shrinkage temperature.
32	As in 31, but as a final step of the preparation of the glue, vinegar was added to the glue: 1/3 vol and ethanol 1/3 vol.	As in 31.	All sorts of gluing, like mending tears, etc.		Change of information about animal and lowering shrinkage temperature.
33	A spoonful of **parchment glue (Nr. 32**) was mixed with a brush full of quite stiff **Hydroxypropyl cellulose** (20% in water), 1:20 and stirred until it was disseminated, then a very small amount of **PVA** was added (1:40) and stirred in, the solution became whitish and finally 6 droplets of **toluene** were added and the solution split.	The "salad dressing" was brushed onto the parchment A sample and left to dry at room temperature.	The mix is meant to consolidate flaking paint layers.		Change of information about animal and lowering shrinkage temperature.
34	**Methylcellulose** from the 1980s was soaked in water and, after swelling, mixed with **PVA** (2 parts MC and 1 part PVA).	The mixture was applied onto the surface of the parchment A. Then the parchment was allowed to dry at room temperature.	To glue elements together.		Lowering shrinkage temperature.
35	Recipe 20 Recipe 32 **Paste** of wheat starch and **parchment glue** was mixed 1:1 vol % and then a bit of **Nipagin** was added.	The mixture was applied onto the surface of parchment A. Then the parchment was allowed to dry at room temperature.	To glue elements together.		Lowering shrinkage temperature.

All treatments were performed in the manner as close as possible to the manner and circumstances back in Wächter's days: all treatments were performed at around 18 °C and a relative humidity of around 50%.

The parchment was made in the Bucharest Leather Institute.[11] The data frame of the procedure of parchment making is given in Table 2. In any case, one skin was used to make all samples, and only in one case was another parchment used.

Table 2: Data frame of the procedure of parchment making

Soaking I:	600% water at 20°C Allowed to stay for 4 hours
Drain Fleshing: manual	
Washing:	400% water at 20°C, drain
Soaking II:	600% water at 20°C, drain 600% water at 20°C 4% salt 0.2–0.4% detergent 3–4 h stirring overnight
Drain	
Liming	400% water at 25°C 4% lime 4% salt 0.3% detergent pH 11.5-12
Post liming	600% float at 25°C 2% lime Allowed to stay for 48 h
Deliming	500% water at 30°C 1% ammonium sulphate Stirring for 40 min; allowed to stay overnight
Washing:	400–600% water at 20–25°C Stirring for 60 minutes, allowed to stay overnight
Rinsing and stretching	

Aged samples were used in the case the treatment was meant for softening. Ageing was done for 60 days with a fluctuating temperature between 10 and 35 °C and a fluctuating relative humidity between 55 and 15% changing every 12 hours, accordingly.

The conservation recommendations by Wächter concerning parchment fall into three main groups, i.e., cleaning or stain removal, softening of hard parchment and bringing elements together, like mending tears or reattaching off-flaking elements of colour, which means adhesion in the wider sense. There are a few other treatments, such as mitigating ink corrosion.

Hypothesis

In general, the hypothesis can be summarized as follows: Wächter's recipes suggest that we are in danger of altering the information we can extract from the material with today's' means and measurements, as the approach to conservation treatments has changed over time.

Specifically, we presume that all water containing applications (as in the recipes listed here) would lower the shrinkage temperature of the parchment, meaning the shrinkage temperature of the collagen fibres, a feature that equates to damaging or lowering the quality of the parchment (being, in a way, a starting point of damage) and is to be avoided in the course of a conservation treatment.[12]

An alteration of the information about the animal can be expected of all recipes that contain DNA themselves (6, 7, 30, 31, 32, 33[13]) and, therefore, add this to the parchment. Where the use of DNA-containing materials is unavoidable, it makes sense to use a form that is as distant as possible from the conservation target. Thus, it is sensible to avoid mammalian glues to repair cultural heritage objects made from mammalian tissues such as parchment; isinglass (fish collagen) is much less likely to obscure a genetic signal from a calfskin parchment than sheep or (worst of all) cattle gelatine. Conversely,

11 *INCDTP - Sucursala Institutul de Cercetari Pielarie Incaltaminte (ICPI); INCDTP - Division Leather and Footwear Research Institute (ICPI), 93, Ion Minulescu St., Sector 3, 031215, Bucharest, Romania.*

12 K. Mühlen Axelsson, D. Sommer, R. Larsen, 'Dimensional studies of specific microscopic fibre structures in deteriorated parchment before and during shrinkage', in: *Journal of Cultural Heritage* 13(2) · April 2012' https://www.researchgate.net/publication/251664963_Dimensional_studies_of_specific_microscopic_fibre_structures_in_deteriorated_parchment_before_and_during_shrinkage (June 2019).

13 Please see Table 1.

in order to conserve fish leather, it would be more sensible to use cattle or rabbit gelatine than isinglass.

The inorganic material to chalk the parchment in the course of its production can be potentially traced geochemically. The use of earth alkali metals in the conservation treatment can interfere with the information of the original material (8, 9, 10).[14]

Furthermore, the presence of Borax might be irritating (26).

A sort of fat tanning can be presumed in recipes 13 and 15.

The application of nylon is described in recipe 18 and the application of eraser powder[15] in recipe 2.

Furthermore, we should take into consideration that such finds would also influence our recent conservation decision-making and choice of conservation material and techniques. If water is a material which endangers parchment so severely, we should either avoid it or find alternative application techniques.

First results

This hypothesis was considered under a philosophical-ethical viewpoint and under a scientific viewpoint. This publication focuses on the latter.

The instrumental analysis should verify whether or not the information carried by the parchment was obscured and, if so, in what way. This would allow for a sort of retranslation of the information gained now into the information which was there originally. In an extreme case, the entire story of the survey of manuscripts by means of instrumental analysis might need to be rewritten.

Peptide mass fingerprinting (PMF) was performed using Matrix-Assisted Laser Desorption/Ionization - Time of Flight (MALDI-TOF) mass spectrometry (MS) to establish the species of animals used to make both the parchment and glue and to assess the level of damage (deamidation) present in the sample due to the manufacturing process.

To carry out the sampling, a previously developed method of the group was used, non-invasive sampling technique (eZooMS), based on triboelectric extraction involving the use of PVC erasers that allows us to interrogate parchment manuscripts without having to use more destructive samples.[16]

Initially, the use of MALDI-TOF mass spectrometry was chosen as it is fast, inexpensive and a useful basic identification tool or screening method. PMF is based on the analysis of one protein (in this case collagen) cut into smaller fragments (peptides) using an enzyme (in this case trypsin). The mass of these peptides measured using MALDI-TOF mass spectrometry creates a profile or "fingerprint" of the protein, which can then be compared to a reference database. With this method, it was possible to determine the species used to make the parchment and also any additional species used to make the glue that might have been applied to the surface.

Our preliminary results are as follows: All samples were identified as coming from goats. With this method, it is also possible to determine a general value of deamidation, a particular type of damage that occurs in the collagen molecule when the skin is exposed to hydrolytic chemical reagents (notably lime) during its production process, which is defined as the Parchment Quality Index (PQI). This is expressed as a percentage; a value of 100% corresponds to no deamidation, and therefore low or no exposure to lime, and a low value points to a more damaged molecule.

In this instance, in which samples were treated with glue, it was found that both the

14 Research into using dust as a source of information for dating and locating a work of art has recently been conducted by the author P. Engel and Th. Prohaska and his team at Montanuniversität Leoben.

15 Product name: Archival Aids Draft Clean Powder DCP3 2 lb can.

16 S. Fiddyment, B. Holsinger, C. Ruzzier, A. Devine, A. Binois, U. Albarella, R. Fischer et al. 2015. 'Animal Origin of 13th-Century Uterine Vellum Revealed Using Noninvasive Peptide Fingerprinting', in: *Proceedings of the National Academy of Sciences of the United States of America*, 112 (49), 15066–71.

parchment and glue are made of the same animal, and thus, it is much harder to determine where the damage is occurring (whether on the parchment as part of its production or from the glue) and will require further data analysis. It is hoped the information that was provided through our analysis will assist conservators in their decision-making and give us a greater understanding of the processes that affect parchment stability and deterioration.

Another suggestion in the conservators' hypothesis had been that the application of some of the products should lower the shrinkage temperature of the collagen. For that, the shrinkage temperature must be measured. This method is also accessible for conservators and is currently performed.

In the meantime, all samples were cut in half and artificially aged in one part; tests will also be run with these to simulate natural ageing.

To conclude: there is much work to be done to understand the way in which the 20th-century conservation methods might have altered the information kept in the material of our cultural heritage, of which only one material and one series of instructions has been discussed here.

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