Hydrolysis and oxidation of collagen in leather and parchment. A deeper insight to the degradation mechanisms at microscopic level.

Ph.D. project at the The Royal Danish Academy of Fine Arts, School of Conservation

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Leather and parchment are amongst the most common artifacts in museums and archives in the world. As such they bear witness about our history and play an important role in our culture. Whereas leather are tanned hides, the definition of parchment is a hide that has been wetted, stretched under tension to dry and scraped thin and where the hair has been removed with alkaline solutions. The difference in definitions between the two materials is therefore to be found in the direction of the fiber structure. In leather the fiber structure is kept in its original three dimensional arrangement, whereas the fibers in parchment are stretched into a two dimensional structure laying parallel with the surface (Reed, 1975). In both cases the composition is based on the fibrous protein collagen type I.

Degradation

High levels of temperature and relative humidity are factors leading to degradation of the collagen. In an unstable climate with high fluctuations in temperature and humidity, the organic material becomes stressed and this may lead to irreversible changes in the chemical and physical structure.

Possible degrading aspects not to be ignored are treatments that the objects may have been and are exposed to in the conservation studios. The use of moisture based compounds (e.g. starch paste) in restoration treatments on leather artifacts may cause irreversible changes of the fiber structure (Svendsen, 2007). Not seldom are parchment objects humidified with water and flattened for aesthetic and readable reasons. This may be very convenient for the moment as the result is a flat readable document, but the risk of causing irreversible damages the object such as gelatinization and loss of text and illuminations is large. An awareness of what effects humidification, flattening and other treatments may lead to in the long run must be spread.

The deterioration of collagen is divided into two main pathways: a hydrolytic breakdown caused by acidic and humid conditions and an oxidative breakdown occurring under dry conditions. As the hydrolytic breakdown leads to cleavage of the peptide bonds, the oxidation process degrades the amino acids into forming carbonyl compounds and crosslinking between the chains. There is research stating that the acid hydrolysis is more aggressive to collagen than what oxidation is. Studies have also shown that the oxidation process may hide the hydrolysis when releasing ammonia in the deamination process of the amino acids (Larsen, 2008). The natural degradation pattern of parchment and leather fibers is very much related to the physical changes that have been observed during shrinkage when heating the fibers in water. Although there are indications that the hydrolysis leads to gelatinized and dissolved fibers that may melt even at room temperature and that the oxidized fibers show signs of fragmented pieces with cracks and brittleness, it is not fully known if the fibers follow significantly different pathways during the course of breakdown.

Oxidative and hydrolytic compounds in the surrounding environment may originate from air born pollutants like ozone, sulphur dioxide and nitrogen oxides, but also in the form of Volatile Organic Compounds (Bowden & Brimblecombe, 2002; ENVIRONMENT Leather Project, 1996; Juchauld et al.,

2007). Quite little is known about thresholds for e.g. acetic acid, formic acid and VOCs on leather and parchment. These compounds may originate from enclosures like show cases, shelves and storage boxes that are in direct or nearby contact with the archival documents or museum objects. Even the objects themselves may emit organic compounds due to previous restoration treatments.

From the 1st of November 2010 the School of Conservation is one of 14 European partners in the EC project MEMORI[1]. One of the main goals of MEMORI is to assess the damage impact of organic acids on cultural heritage objects. Research will be focused on observing impact doses and degradation effects on different types of materials by performing controlled accelerated exposures of selected air pollutants. The School of Conservation is in charge of the work package directed to leather and parchment and in which work package I am functioning as a research assistant. My Ph.D. project will be very much associated with the work and results in the MEMORI project; a collaboration in this way is a significant opportunity of gaining and sharing knowledge in an international project with my own research. The MEMORI project will go on for three years until the end of 2013.

Objectives

The thesis is based on the hypotheses that hydrolysis and oxidation of leather and parchment result in different characteristic appearances of the collagen and that it is possible to differentiate between the two breakdown categories by studying the morphology of the fibers. Furthermore, analyses will be conducted on different areas on single fibers. The theory that sites of unstable and charged amino acids residues are more prone to degradation than areas consisting of stable hydrophopbic amino acid residues will be evaluated by deeper research into different characteristic areas found in single fibers. The research will focus on microscopic analyses used in the IDAP[2] network, such as fiber assessment and measurement of the hydrothermal stability of the collagen with the Micro Hot Table-method (MHT) together with comparative analyses at other structural levels: Atomic Force Microscopy (AFM) at nanoscopic level, High Performance Liquid Chromatography (HPLC) at molecular level as well as Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) etc. The outcome will be a simple tool that can be used commonly in the conservation studios without being obliged to expensive analyses.

[1] Measurement, Effect Assessment and Mitigation of Pollutant Impact on Movable Cultural Assets. Innovative Research for Market Transfer. www.memori-project.eu
[2] Improved Damage Assessment of Parchment. www-idap-parchment.dk

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