Journal of Cultural Heritage 15 (2014) 373–381

Available online at ScienceDirect www.sciencedirect.com

Elsevier Masson France EM|consulte www.em-consulte.com/en

Original article

The influence of pollutants on accelerated ageing of parchment with iron gall inks

Michaela Ciglanská [a], Viera Jančovičová [a,*], Bohuslava Havlínová [a], Zuzana Machatová [a], Vlasta Brezová [b]

[a] Department of Graphic Arts Technology and Applied Photochemistry, Institute of Polymer Materials, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, SK-812 37 Bratislava, Slovak Republic
[b] Department of Physical Chemistry, Institute of Physical Chemistry and Chemical Physics, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, SK-812 37 Bratislava, Slovak Republic

ARTICLE INFO

Article history:
Received 18 June 2013
Accepted 19 September 2013
Available online 14 October 2013

Keywords:
Parchment
Iron gall inks
Optical properties
UV/VIS spectroscopy
FTIR spectroscopy
EPR spectroscopy

ABSTRACT

Moist heat (100 °C in closed vessels) and pollutants (SO_2 or NO_x, 100 °C) techniques of accelerated ageing were applied in stability investigation of iron gall inks on parchment. The measured characteristics on parchment samples coated with inks (made of iron(II) sulfate and gallic acid or tannic acid in various ratios) reflected their chemical, optical and spectroscopic attributes. Decrease of surface pH values was measured for all samples, especially after ageing with SO_2. The results obtained, comparing the non-aged samples with those aged upon heat and pollutants, revealed the decrease of lightness L^* and the increase of chromatic coordinate b^* for all six ink layers. These differences in b^* were dominantly reflected in values of total color difference (ΔE^*_{ab}, CIE $L^*a^*b^*$). The variations in UV/VIS reflectance spectra and ΔE^*_{ab} evidenced the considerable damage of inks exposed to accelerated ageing, especially for inks prepared with excess of acid to iron. FTIR spectroscopic measurements of parchment showed that accelerated ageing procedures caused changes in structure and arrangement of collagen, and the formation of oxidation products in parchment during the accelerated ageing was stimulated by presence of inks. EPR spectra of parchment coated with inks showed the paramagnetic signals of various Fe(III) species ions in different coordination.

1. Introduction and research aims

Materials constituting the cultural heritage object are subjected to changes upon time, due to the interaction between the object and physical factors (light, temperature, relative humidity, oxygen, particulates), chemical factors (atmospheric oxygen, various pollutants), and biological agents (bacteria, fungi, insects, mold) [1]. Parchment is a collagen-based, historically important biomaterial that contains many layers of information, from text written on the surface, to the structure of the material itself [2,3]. The degradation of historical parchments is often attributed to storage conditions, although other factors may also accelerate the decay of collagen within the parchment (harsh cleaning, extreme variations in pH during manufacturing techniques) [3]. Three major degradation paths are considered for collagen, i.e., hydrolysis, oxidation and denaturation [4]. The degradation of parchment starts at tripeptides in clusters of charged amino acids, i.e. acidic breakdown causes hydrolysis of the peptide bonds in the peptide chains, and amino end groups are generated. These may attack carbon atoms in peptide side-chains coupled with polar groups formation, particularly carboxylic acid derivatives [5]. The oxidative breakdown processes of parchment are based on action of heat, light, humidity and chemical pollutants [6,7].

Iron gall inks were the most commonly used writing and very popular drawing media since antiquity. They were produced by mixing aqueous solutions of iron(II) sulfate with extracts of gall nuts [8,9]. Many iron gall inks have a corrosive nature and tendency to undergo color change from black to brown, often fading quite significantly. Numerous documents, manuscripts and artworks now stand in danger of deterioration, while others are still in excellent condition [10–12]. Certain combinations of environmental storage conditions (especially SO_2 and NO_x pollutants), composition of the inks and used supports result in a partial or total loss of the paper or parchment [13,14]. The historical parchment samples represent unique, very complex systems, requiring detailed

Abbreviations: AI, Amid I band; AII, Amid II band; ATR, Attenuated Total Reflectance; ΔE^*_{ab}, Total color difference; EPR, Electron Paramagnetic Resonance; FTIR, Fourier Transform Infrared; GA, Gallic acid; NIR, Near Infrared; OD, Optical Density; R, Reflectance; RH, Relative Humidity; SW, Magnetic field sweep; TA, Tannic acid; UV/VIS, Ultraviolet/Visible; XRF, X-Ray Fluorescence.

* Corresponding author. Tel.: +4212 5932 5227; fax: +4212 5935 5224.
E-mail addresses: michaela.ciglanska@stuba.sk (M. Ciglanská), viera.jancovicova@stuba.sk (V. Jančovičová), bohuslava.havlinova@stuba.sk (B. Havlínová), zuzana.machatova@stuba.sk (Z. Machatová), vlasta.brezova@stuba.sk (V. Brezová).

1296-2074/$ – see front matter © 2013 Elsevier Masson SAS. All rights reserved.
http://dx.doi.org/10.1016/j.culher.2013.09.004

Table 1
The composition of ink formulations used in the study.

Ink sample	Gallic acid monohydrate [g][a]	Tannic acid [g][a]	$FeSO_4 \cdot 7H_2O$ [g][a]	Gum arabic [mL][b]	Molar ratio	
					Iron:GA	Iron:TA
A	0.75	–	6.1	33.5	5.5:1	–
B	0.75	–	1.12	33.5	1:1	–
C	0.75	–	0.2	33.5	1:5.5	–
D	–	4.1	3.67	33.5	–	5.5:1
E	–	4.1	0.67	33.5	–	1:1
F	–	4.1	0.12	33.5	–	1:5.5

GA: gallic acid; TA: tannic acid.
[a] Gallic/tannic acids were dissolved in 20 mL of deionized water, $FeSO_4 \cdot 7H_2O$ was added and deionized water was refilled to obtain 50 mL of solution.
[b] Concentration of aqueous solution of gum arabic 78.5 g L^{-1}.

and non-destructive analysis before the conservation treatments [4,12–15]. Consequently, an intensive attention was focused on the application of non-invasive spectroscopic techniques (UV/VIS/NIR, FTIR, Raman, EPR) providing valuable information on the actual state of historical parchments [10,12–16]. With aim to avoid undesired effects of conservation, these techniques were successfully applied also for the simulation of ageing processes using new laboratory parchment samples [12–15].

The aims of our study were oriented not only to characterize the parchment artificially aged (also coated with model inks) by a combination of heat and pollutant, but additionally, the methods and techniques were applied in order to evaluate the deterioration of parchment upon accelerated ageing simulating the real parchment damage during the long-term storage. The parchment samples were analyzed by surface pH measurements, colorimetric techniques and spectroscopic methods (UV/VIS, FTIR, EPR spectroscopy).

2. Materials and methods

2.1. Materials

The used parchment was goatskin grounded on both sides (GARA TZL PLUS, Tannery Otrokovice, Czech Republic). The results of our XRF analysis (XRF spectrometer X-MET 5000 Oxford Instrument) proved the negligible concentration of Ca, Fe and Cu in tested samples. Gallic acid monohydrate, tannic acid, and gum arabic were purchased from Sigma-Aldrich, ferrous sulfate heptahydrate from Lachema (Brno, Czech Republic). NO_x gas (NO + NO_2; 2000 ppm NO_x in synthetic air) was obtained from Messer Tatragas and SO_2 gas (purity of 99.5%) from Air Products.

2.2. Preparation of ink samples

The iron gall inks were prepared by mixing of gallic acid (GA) monohydrate or tannic acid (TA), iron(II) sulfate heptahydrate and gum arabic in deionized water using the recipes summarized in Table 1.

The reaction mixtures were exposed to air with occasional stirring for one hour. Subsequently the prepared inks **A**–**F** were applied on parchment samples of size 2 × 4 cm (0.1 mL of the solution was unilaterally applied on the whole area of parchment) and dried on air at room temperature. Ten pristine parchment samples and ten ink-coated samples using each ink from series **A**–**F** were prepared for evaluation; five measurements were carried out on each sample.

2.3. Accelerated ageing

Three types of accelerated ageing were used:

(i) accelerated ageing was performed in closed vessels (100 mL) at temperature of 100 °C according to the method described in the standard ISO 5630-5 [17]. The ageing was performed in a multifunctional oven APT Line Series FED with the regulation R 3.1 by Fisher Scientific for 1, 3, 7, 14 and 28 days. Immediately before ageing, the samples were conditioned at 23 °C and 50% relative humidity (RH) for 24 h;
(ii) the second type of ageing was performed in atmosphere with SO_2. The vessels with samples were flushed with SO_2 gas for 40 s (flow rate 11.0 mL s^{-1}) before ageing, consequently closed and aged at 100 °C in the same oven as mentioned in (i). The final ageing period was 28 days;
(iii) the last type of ageing was performed in NO_x atmosphere. The procedure was carried out under the same conditions as in (ii), only the vessels were flushed with NO_x (40 s, flow rate 16 mL s^{-1}) before ageing. The final ageing period was 28 days.

2.4. Characterization of parchment

The characterization of parchment samples (surface pH, colorimetric measurements, UV/VIS, FTIR) was performed at temperature range 20–23 °C and at relative humidity 30–35%.

2.4.1. Surface pH

The surface pH measurements were performed using special electrode (Jenway, model 3510) on the parchment side with the ink [18].

2.4.2. Colorimetric measurements

CIE $L^*a^*b^*$ system was used to evaluate the color changes. The colorimetric coordinates of samples (L^*, a^*, b^*) were obtained by means of Spectrophotometer Spectrodens (Techkon, illumination D50, standard observer 2°).

The total color difference ΔE^*_{ab} was calculated from Eq. (1) [19],

$$\Delta E^*_{ab} = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (1)$$

where values ΔL^*, Δa^* and Δb^* are the differences between relevant values attributed to aged and non-aged samples.

2.4.3. Ultraviolet/Visible (UV/VIS) spectroscopy

The reflectance spectra in UV/VIS region (230–900 nm) were measured with the fiber optics spectrophotometer system Ocean Optics consisting of Hi-Res spectrometer HR 4000CG-UV-NIR (standard reflectance accessory with 45°/45° geometry). For each measurement, the detector was calibrated to the blank parchment. Original reflectance (R) spectra were transformed into optical density (OD) using Eq. (2):

$$OD = -\log R \quad (2)$$

2.4.4. Fourier Transform Infrared (FTIR) spectroscopy

The FTIR spectra were measured with the FTIR spectrophotometer Excalibur Digilab FTS 3000MX, USA, using the ATR adapter