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Investigation of Damaged Paper by Ink Corrosion

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The investigation of cotton fibers sheets treated with different historical writing inks: Pfalz ink from red wine (ink-1, pH 3.51), Ink from the oak's bark extracts (ink-2, pH 3.69); Iron-gall ink (ink-3, pH 1.66), Black ink with iron(II) sulphate (ink-4, pH 1.52), Black ink with copper(II) sulphate (ink-5, pH 2.14), Logwood tree ink (ink-6, pH 5.73), German recipe A (iron(II) sulphate) (ink-7, pH 1.94), German recipe B (iron(II) sulphate) (ink-8, pH 1.62) was performed using FTIR spectroscopy. The paper and ink treated paper samples were artificially aged (accelerated thermal and photo ageing) also analyzed and the results compared with the non-treated ones. The study focus was on the spectrum range between 1500 cm^{-1} and 1900 cm^{-1}, where the products of the paper ageing appear as various carbonyl groups. After immersing paper to inks with metal ions, the increase of absorption at 1713 cm^{-1} – 1745 cm^{-1} was observed. Also, the drastic decreasing of polymerization degree of ink treated samples was estimated.

Keywords: paper, writing ink, ageing, FTIR, carbonyl vibration, polymerization degree.

INTRODUCTION

A significant part of culture heritage was recorded with different types of inks. The large variety of different recipes and the compositional diversity of the natural raw materials result in a diversity of distinguishable degradation mechanisms leading to changes in colour after time and, occasionally, resulting in ink corrosion. This process ends in a complete degradation of the paper or parchment [1 – 5]. The reactions between ink and the carrier materials are influenced by environmental and storage conditions, especially by changes in temperature, light and humidity. Two principal causes are usually considered to be responsible for the paper degradation. The first one is the high acidity of some inks that leads to hydrolytic splitting of the cellulose (formation of acid). The second one is the presence of soluble and mobile metal ions that may act as catalysts for oxidative decomposition of the cellulose. This oxidation involves the intermediate formation of radicals ($O_2^{\bullet}$, $HOO^{\bullet}$) reaction of metals ions with $HOO^{\bullet}$ in acidic medium that leads to the formation of H_2O_2, which in its turn can further oxidize the paper [6 – 10].

Vibrational spectroscopy IR and Raman spectroscopy enables a print to be studied "as is" and thus provides information on the actual paper-ink interactions. The spectra show certain bands, i. e., characteristic vibrations, which are typical of particular groups of atoms and which are defined by definite ranges of frequencies and intensities in the IR spectra. The recent results published demonstrated clearly that IR spectroscopy is indispensable tool for the characterization of paper [11 – 16]. Other advantages include detail molecular characterization, minimal demands for the sampling environment and easy of sampling preparation.

Before we can fully understand the ink-corrosion mechanism, we must answer a lot of questions concerning the degradation of paper material, ink composition and paper-ink system during the ageing process. The main object of this work is to investigate the influence of ink composition and ageing to progress of ink corrosion.

EXPERIMENTAL

The different writing ink samples were prepared using different recipes. The details of ink preparation can be found in [17]. The inks Pfalz ink from red wine (ink-1, pH 3.51), Ink from the oak's bark extracts (ink-2, pH 3.69); Iron-gall ink (ink-3, pH 1.66); Black ink with iron(II) sulphate (ink-4, pH 1.52), Black ink with copper(II) sulphate (ink-5, pH 2.14); Logwood tree ink (ink-6, pH 5.73); German recipe A (iron(II) sulphate) (ink-7, pH 1.94), German recipe B (iron(II) sulphate) (ink-8, pH 1.62) were used for paper treatment. The prepared cotton fibres paper sheets (30 mm × 60 mm) were immersed into a solution of the different inks and artificially aged. The samples of the paper and paper-inks were artificially aged (accelerated thermal and photo ageing). Heated samples were aged 240 h (10 days) or 480 h (20 days) at constant temperature of 105 °C in an oven. UV samples were treated 100 h with DRT-400 mercury lamp. Chamber samples were aged 30 h in a reaction chamber with a mercury lamp, thermostat (40 °C) at constant humidity (RH 65 %). The FTIR measurements were performed using a Perkin-Elmer FTIR Spectrum BX II spectrometer. A total of 20 scans were taken for each sample with a resolution of 4 cm^{-1}. The mixture of paper fibers and KBr was pressed into a disk for FTIR measurement. The area of the CH vibration band (2900 cm^{-1}) of the initial spectrum, namely, the integral in the frequency range 2800 cm^{-1}– 3000 cm^{-1} was the normalization factor for all absorbance values. ISO standard 5351/04 was followed for viscosity and degree of polymerization DP determination [18, 19]. The glass viscometer (capillary 0.86 mm) and cupric ethylenediamine (CED) as solvent were used for the measurements. The cold-water extraction method was used for pH measurements. The small amount of samples (0.002 g) was suspended in distilled water. Surface pH of the paper was determined by using InLab 423 electrode

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and the pH meter Mettler-Toledo MP220 was employed for measuring pH values of suspended samples.

RESULTS

The aim of using FTIR is to measure the change of paper surface composition of fibres after ink treatment and artificial ageing. The spectrum of aged and treated paper is not easy to resolve, because it consists of many overlapping bands. The most informative spectral region of cellulose spectra is between 1500 cm^{-1} and 1900 cm^{-1}. The literature does not provide a systematic and congruent analysis of a complex vibration pattern of various carbonyl groups evolved during paper ageing. Lojewska et al [14, 15] ascribed the most intense maxima to aldehyde/carboxyl groups (1732 cm^{-1}, 1745 cm^{-1}) and conjugate carbonyl groups (1620 cm^{-1}). Carbon atoms in various oxygen environments (–COOH, –CHO, –CO) are the products of cellulose partial oxidation and hydrolysis. Thus, a parallel toward oxidation, occurring predominantly on various C–OH groups on various glucopyranose rings, is expected to give a variety of different carbonyl groups, while a simpler reaction which is hydrolysis – gives mainly aldehyde groups on terminal rings.

At first, the model paper was investigated after thermal and photo ageing. Infrared spectra in region 1500 cm^{-1}–1900 cm^{-1} of paper samples are shown in Fig. 1. The broad absorption bonds in all spectra around 1640 cm^{-1} indicate the presence of adsorbed water on the surface of samples. The all treated samples give similar FTIR spectra, very close to pure cellulose spectra.

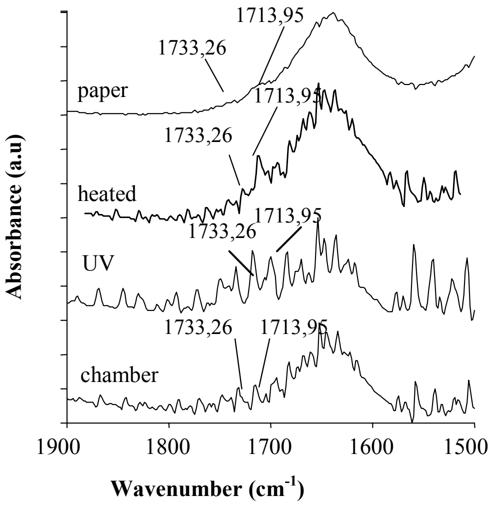

Fig. 1. FTIR spectra of paper and aged paper samples

However, according to the origin of the bands, it is seen that thermally and UV treated samples are slightly different. For instance, IR spectrum of the sample thermally heated 240 h at 105 °C temperature contains the more intensive bands attributable to the –CO and –CHO stretching at 1713 cm^{-1} and 1733 cm^{-1}.

The paper samples were immersed to the inks (1– 8) and dried at room temperature. The inks-paper samples were aged at 105 °C, treated by UV lamp or kept in a chamber. The IR spectra are shown in Figs. 2 – 5. The FTIR spectra of all ink-paper samples kept in a chamber are non informative due to the big water absorption on a paper surface. The IR spectra of samples treated with inks (1, 2) are close to paper IR spectra data. The slight increase of absorbance intensity at 1713 cm^{-1} was obtained after heating 240 h at 105 °C and UV treatment.

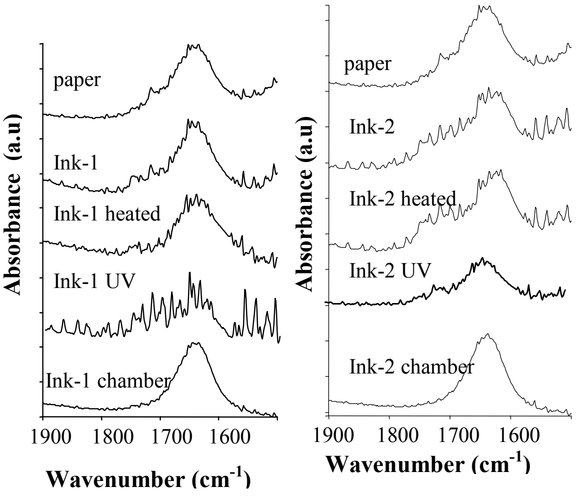

Fig. 2. FTIR spectra of samples of paper with ink-1 and ink-2

While, in the spectra of the ink (3 – 8) treated papers the intensive prominent bands appear at wavenumbers 1713 cm^{-1}, 1733 cm^{-1}, and the band at 1745 cm^{-1}. This bands could be attributed to the functional –CO, –CHO and –COOH groups. Also, the –CHO (1733 cm^{-1}) formation was accelerated by the photo ageing treatment of paper immersed in inks (3 – 6) (Fig. 3 and Fig. 4).

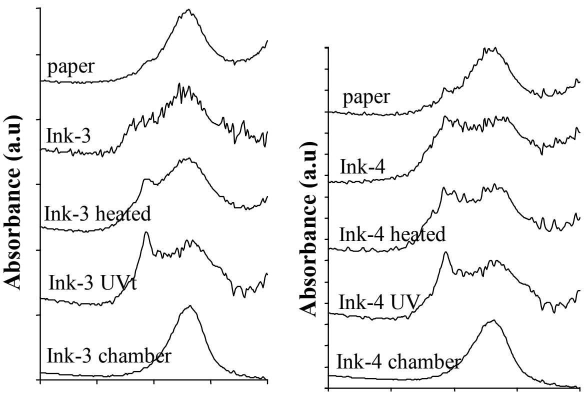

Fig. 3. FTIR spectra of samples of paper with ink-3 and ink-4

Paper acidity/alkalinity could be estimated using some arbitrary procedures, by extraction and subsequent titration. A comparison of surface pH of the paper with inks treated paper samples has shown that, in all cases, the pH of ink treated samples had dropped below non-treated paper value pH 6.5 (Fig. 6). The decrease is relevant to the ink compositionthe the pH value. The pH value of ink-6 sample was obtained 6.09, as the initial ink solution value was pH 5.75. While the ink-8 (pH 1.62) treatment caused an increase in the pH of the paper until 3.29. After 240 h heating at 105 °C the slight decreasing of pH was obtained in all cases.

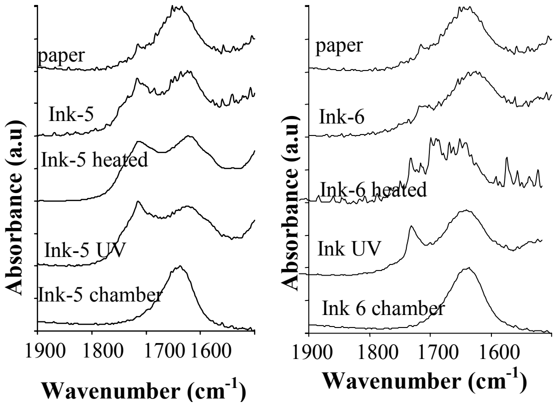

Fig. 4. FTIR spectra of samples of paper with ink-5 and ink-6

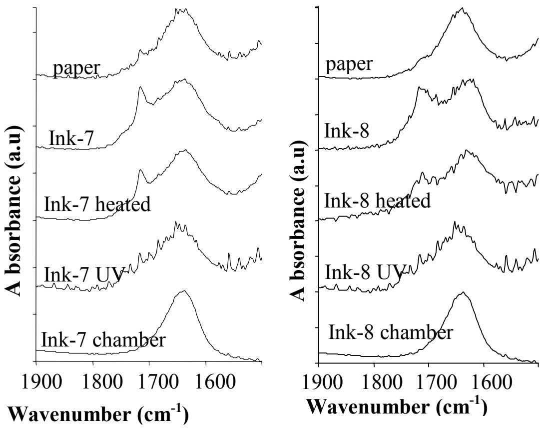

Fig. 5. FTIR spectra of samples of paper with ink-7 and ink-8

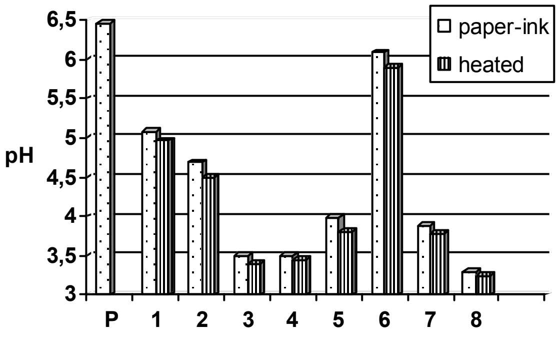

Fig. 6. pH measurements of paper (P), treated ink (1 – 8) paper samples and heated samples

The depolymerization of cellulose – the breaking of the linkages between the monomer units leading to the formation of smaller polymer chain – can be used by acid or alkaline hydrolysis and radical oxidation reactions. Viscometric determination of the degree of cellulose polymerisation (DP) was performed according to standard procedure, using fresh cupriethylenediamine solvent. The degree of polymerisation was calculated from the intrinsic viscosity using the Immergut equation ($[\eta] = Q\,DP\alpha$, $Q = 1.33$ ml/g and $\alpha = 0.905$). The data of cellulose polymerization degree are shown in Fig. 7.

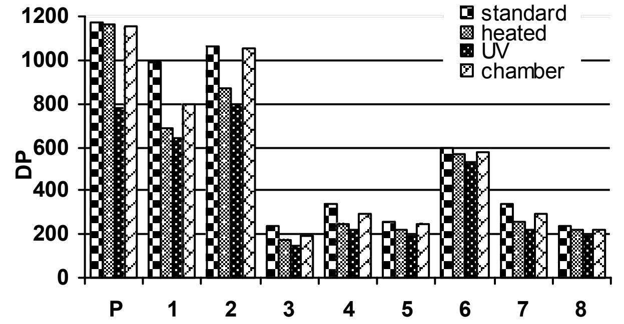

Fig. 7. Degree of polymerisation (DP) of paper (P) and inks (1–8) heated 480 h at 105 °C, UV and in chamber treated samples

As we can see from the obtained results, the depolymerisation level of heated and treated in a chamber paper is lover than UV treated samples ones. But the extensive degradation of paper was observed after treatment of paper with inks. The DP of sample treated with ink-1 decreased from 1176 to 989, while with inks-3 and ink-8 to 241. Also, the decreasing of DP values of heated and UV inks-paper samples was obtained.

CONCLUSIONS

The influence of ink constituents on the cellulose degradation by ink corrosion can be evaluated by FTIR after artificial ageing. Variations in absorption appeared in the region between 1500 cm^{-1} and 1900 cm^{-1}. This region is characteristic of carbonyl and carboxyl groups stretching vibration. Increasing of absorption intensity at 1713 cm^{-1}–1745 cm^{-1} is attributed to cellulose oxidation or hydrolytic products and depends on ink composition. The pH decreasing of paper-ink samples is relevant to pH value of ink composition The drastic decreasing of polymerization degree of samples with inks containing metal ions was estimated. The inks containing metal ions accelerated the paper degradation.

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