

STABILISATION OF CORROSIVE IRON GALL INKS

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Abstract

Leonardo Da Vinci, J. S. Bach and Victor Hugo are just a few artists, who executed their works with iron gall ink. It has long been known that iron ions and acids in these inks induce severe damages to historical artefacts. In this contribution we demonstrate that transition metal content of historical iron gall inks varies greatly, with molar ratio of copper to iron as high as 0.7. Due to its superior catalytic activity, it is copper, not iron which contributes most to the extensive oxidative decay of many documents containing copper-rich iron gall inks. An effective stabilisation of ink corrosion is achieved by peroxide decomposer tetrabutylammonium bromide.

Introduction

Iron gall ink is probably the most important ink in the Western history. While a number of different historical recipes have been passed down to us,¹ they share common colour-forming ingredients: gallic acid from tannins and iron ions. Unfortunately, these components induced severe damage or even complete destruction of numerous historical artefacts (Figure 1). Thus 60-70% of Leonardo da Vinci's oeuvre shows signs of deterioration.²

The two main reasons for iron gall ink corrosion have been identified to be acid hydrolysis and oxidation, catalysed by ferrous ions.³ The deleterious effects of the former have been recognized already in the 19th century, when the alum-rosin sizing process was found to be responsible for the low stability of machine-made papers. A century later, libraries and archives are faced with kilometres of shelves of rapidly decaying "acidic paper". Due to the immense proportions of the "acidic paper" problem, long-term preservation of all of the endangered materials is hardly feasible. A partial solution may be the reformatting of documents, by either microfilming or digitalisation, or the so-called deacidification. The latter procedure is a chemical treatment, during

which the “acidic paper” is immersed into a solution of alkalis.⁴ As acids are one of the culprits for the corrosiveness of iron gall ink, the same treatment may be applied for a partial stabilization of iron gall ink containing paper.



Figure 1. Manuscript by Galileo Galilei, destroyed by iron gall ink corrosion (Collection Nationaal Archief, The Netherlands).

In addition to acids, iron gall inks contain a substantial amount of iron ions. Ferrous ions react with peroxides produced during oxidation of organic materials, thus releasing extremely reactive hydroxyl radicals. Reduction of Fe^{3+} by many organic compounds, superoxide anions and even peroxides, allow these reactions to be repeated in a cyclic fashion, resulting in extensive oxyradical damage. The primary reaction leading to the production of hydroxyl radicals had been used by H. J. H. Fenton for oxidation of tartaric acid in 1876⁵ and is since then referred to as the Fenton reaction.

In order to prevent oxidative decay of substances, antioxidants are usually employed. Therefore, an effective stabilisation of iron gall ink containing paper may be achieved by addition of alkalis to combat acid hydrolysis, and antioxidants to prevent oxidation. In the present study, the use of an antioxidant tetrabutylammonium bromide for the stabilisation of iron gall ink containing paper is examined.

Results and discussion

The only knowingly effective antioxidant, which can be used for stabilisation of ink decay is the iron chelating agent *myo*-inositol hexaphosphate (phytate),⁶ theoretically

doubling the lifetime of deacidified iron-containing paper.⁷ Due to its strong stabilising potential, the method has been quickly adopted and developed to a stage, where it can be considered safe to be used by conservators.⁸ Unfortunately, phytate is only able to decrease the catalytic properties of iron ions, while some other transition metal ions, most notably copper, retain their catalytic properties, thus still contributing to corrosiveness of the ink. An insight into the transition metal content of historical iron gall inks is imperative, in order to develop and adequately evaluate a stabilisation treatment for iron gall ink containing documents.

To achieve this, we have used a non-destructive in-air PIXE method for analysis of 99 historical documents from the collection of Slovenia's National and University Library and from the Regional Archives of Maribor, ranging from 14th to 20th century. The results demonstrate that inks containing substantial amounts of copper were used throughout the time span covered by our study. The molar ratio of copper to iron surpassed 10% in 32 manuscripts, while it was higher than 60% in 6 documents (Figure 2). Molar ratios of other potential catalysts were lower, not exceeding 4.6% for chromium, 5.8% for manganese, 10.1% for cobalt and 1.9% for nickel.

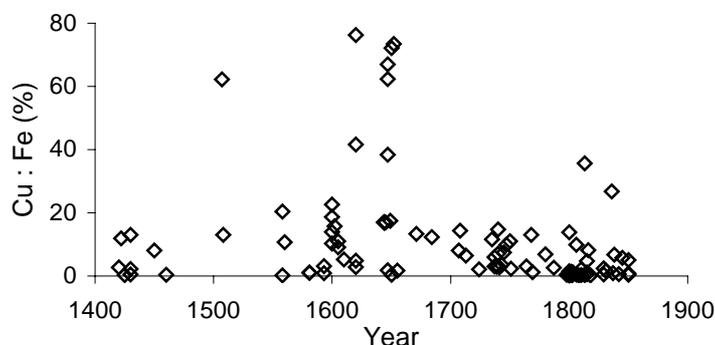


Figure 2. Molar ratios of Cu:Fe in historical iron gall inks, as determined with in-air proton induced X-ray emission.

Such surprisingly high quantities of copper ions in historical inks are disturbing, as the caretakers of the paper-based cultural heritage are familiar with the rapid deterioration of historical paper containing green copper pigments such as basic copper acetate called verdigris.⁹ However, it was suggested that in low concentrations, in the presence of ferrous ions, copper ions inhibit hydroxyl radical production in acidic pH regions.¹⁰ Knowing that the molar ratio of Cu: Fe in iron gall ink may be as high as 0.7,

it was therefore of interest to examine the catalytic effect of mixtures of Fe and Cu in the Fenton-like system at pH values close to neutral, imitating the macromolecular environment of cellulose in paper after deacidification.

Purified cellulose sheet (Whatman filter paper) was impregnated with the corresponding mixtures of FeCl_3 and CuCl_2 (the total concentration of metals remaining the same, $0.0151 \text{ mol L}^{-1}$) and its degradation rate during accelerated aging at $80 \text{ }^\circ\text{C}$, 65% RH was determined using viscometry. The rate was calculated using the Ekenstam model.¹¹ From Figure 3 it is evident that at given conditions, the catalytic effects of iron and copper are additive, leading to the conclusion that the higher the content of copper in iron gall inks, the more corrosive the ink is likely to be, once deacidification had been performed.

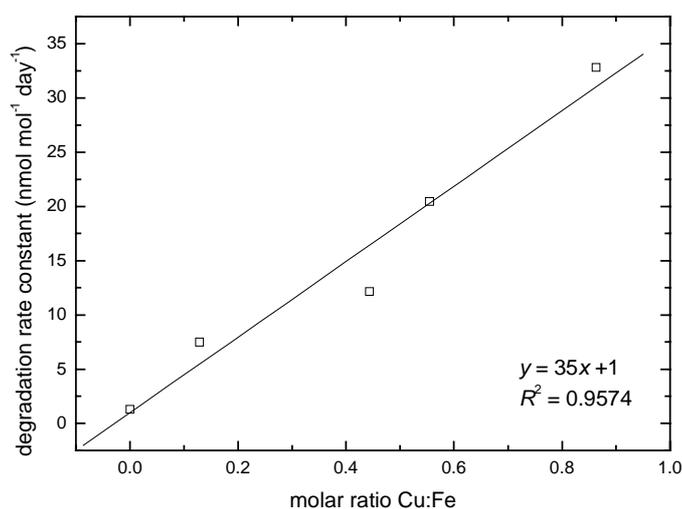


Figure 3. Rates of degradation of CaCO_3 -deacidified cellulose at $80 \text{ }^\circ\text{C}$, 65% RH, containing the transition metals Fe and Cu in ratios as indicated.

Given the high copper content of some historical inks and its superior catalytic activity, the suitability of iron complexing agent phytate for stabilisation of iron gall inks rich in copper was questioned. Three different model iron gall inks, with a Cu:Fe molar ratio 0.01, 0.38 and 0.70 were applied to a model paper and treated either by deacidification with calcium bicarbonate, or deacidification combined with the antioxidant phytate.¹² Bromide containing paper was obtained by immersing deacidified model paper into a 1% aqueous solution of tetrabutylammonium bromide. The latter, like the better-known

iodide is thought to act as a catalytic peroxide decomposer, and is thus capable of interfering with the oxidative decay irrespective of the type of transition metal.

The results presented in Figure 4 demonstrate that phytate does stabilise inks, which contain a substantial amount of transition metals other than iron and may thus continue to be used for stabilisation of historical inks. However, the superior stabilising potential of the newly proposed antioxidant bromide over traditional deacidification and phytate treatment for all selected model inks is evident. In addition to stabilising paper containing iron gall inks, bromide is capable of inhibiting degradation of the paper itself in alkaline environment (Figure 4), thus offering additional benefits of the proposed potential stabilisation method.

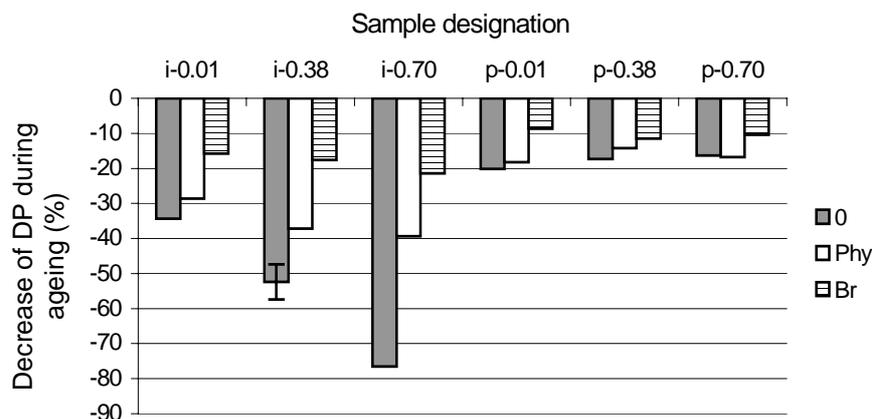


Figure 4. Effect of stabilisation treatments on the decrease of DP of ink containing (i-) and surrounding (p-) paper. Deacidification was performed by immersion into $\text{Ca}(\text{HCO}_3)_2$ solution, and 0 - using no antioxidant; Phy - using phytate and Br - using bromide. Iron gall inks, with Cu:Fe molar ratio 0.01, 0.38 and 0.70 were used. Error bar represents relative standard deviation.

Namely, the selected antioxidant may be used to improve the effectiveness of the most often used conservation process, deacidification. In September 2003, a patent covering the application of halides for stabilisation of iron gall inks and deacidification of paper has been submitted by ZFB, Zentrum für Bucherhaltung GmbH (Leipzig, Germany), a partner in the EU funded project InkCor, under the auspices of which this study was performed.

Conclusions

An extensive survey of historical documents was performed. Using advanced methods of non-destructive analysis, it is shown that transition metal content in historical iron gall inks varies greatly, with molar ratio of copper to iron as high as 0.7. This finding is of high importance as a superior catalytic activity of copper vs. iron in oxidative reactions leading to degradation of paper is also demonstrated. As a result, it is copper, not iron which contributes most to the extensive oxidative decay of many documents containing copper-rich iron gall inks. Effective stabilisation of ink should therefore focus on antioxidants, capable of inhibiting corrosion catalysed by a variety of transition metals, not ferrous ions alone, which has been the aim of the researchers until now. A novel method achieving a superior stabilisation of ink corrosion is proposed using a peroxide decomposer, tetrabutylammonium bromide thus enabling historical documents of immense value to be successfully preserved.

Experimental

Paper samples used were purified cotton linters cellulose sheets (Whatman filter paper no. 1; 86.0 g m⁻², degree of polymerisation (DP): 2630, RSD 0.74%.

Three model inks were made that closely resemble typical transition metal ion compositions, as obtained by PIXE analysis of 99 historical documents. The ink solutions contained Cu²⁺ and Fe²⁺ in the Cu:Fe molar ratio of 0.01, 0.38 and 0.70 as well as minor concentrations of Cr, Mn, Co and Ni, the summary concentration of transition metal ions being the same (Table 1). Inks were applied using a Roland plotter DXY 990 with a 0.6-mm pen at the speed 5 cm s⁻¹.

Table I. Composition of model inks.

<i>c</i> (g L ⁻¹)	ink designation		
	i-0.01	i-0.38	i-0.70
gum Arabic	3.14	3.14	3.14
Tannin	4.92	4.92	4.92
Cr(NO ₃) ₃ ×9H ₂ O	0.1846	0.0000	0.0000
MnSO ₄ ×H ₂ O	0.0984	0.0248	0.0593
FeSO ₄ ×7H ₂ O	3.5827	2.9972	2.3864
CoSO ₄ ×7H ₂ O	0.2721	0.0252	0.0461
NiSO ₄ ×7H ₂ O	0.0375	0.0000	0.0000
CuSO ₄ ×5H ₂ O	0.0188	1.0212	1.5002

Viscometric determinations of the degree of polymerisation (DP) were performed according to the standard procedure,¹³ using fresh cupriethylenediamine solvent (Carlo Erba, Milano). DP was calculated from the intrinsic viscosity using the equation¹⁴ $DP^{0.85} = 1.1 \cdot [\eta]$.

Calcium ammonium phytate solution was prepared by adding 2.28 g of phytic acid (40%, Fluka) to 1 L of distilled water, after which the pH was adjusted to 5.8 by the addition of aqueous ammonium hydroxide solution. Samples containing iron gall ink were immersed for 15 min, in two successive baths of the calcium ammonium phytate solution, dried and deacidified by immersion into aqueous solution of $\text{Ca}(\text{HCO}_3)_2$ (Riedel de Haen) 0.01 mol L^{-1} . Bromide containing paper was obtained by immersing deacidified model paper into 1% aqueous solution of tetrabutylammonium bromide (Fluka).

Samples containing iron gall ink were pre-aged for 3 days at 70 °C and 50% RH, treated and aged for additional 12 days at 90 °C with a changing relative humidity, cycling between 35–80% RH every 3 h in a Vötsch VC 0020 ageing oven.

Selected historical iron gall ink documents were analysed with the in-air PIXE experimental arrangement installed at the Institute Jožef Stefan, Ljubljana, Slovenia. The documents were mounted, one at a time, on the positioning platform and the chosen ink spots on the sample were irradiated by protons. The 2-MeV proton beam passed a 8 μm exit Al foil, separating the accelerator vacuum system from the air, and traversed 9 mm of air before hitting the analyzed spot. The beam diameter was 0.7 mm as defined by the pinhole carbon collimator. The Si(Li) detector was positioned at 45° to the proton beam at the distance of 48 mm from the target. The exact placement of the analyte was achieved by an automatic positioning system using a laser beam. A video camera was used for the control of set-up geometry in the direction of the proton beam (z direction). The positioning platform enables precise movements of the document in the x and y direction in order to be able to irradiate the selected point on the document. The mass fractions of chemical elements Si to Pb was determined, including the typical components of iron gall ink Fe, S, K, Cu, Zn, Co, Mn, and Ni. The error in determination is estimated to be approximately ± 20 ppm. The analyses were performed non-destructively as no visible damage was observed on the irradiated documents.

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Povzetek

Leonardo Da Vinci, J. S. Bach in Victor Hugo so le nekateri izmed avtorjev, ki so pri svojem ustvarjanju uporabljali železo-taninsko črnilo. Že dolgo je znano, da visoka vsebnost kislin in železovih ionov v črnilu močno poškoduje papirni nosilec zapisa. V pripevku je pokazano, da vsebnost kovin prehoda v historičnih dokumentih močno niha, z množinskim razmerjem bakra proti železu do 0.7. Glede na bistveno višjo katalitsko aktivnost bakra, so torej bakrovi in ne železovi ioni poglavitni vir oksidativne razgradnje številnih dokumentov. Učinkovito stabilizacijo železo-taninske razjede smo dosegli z dodatkom tetrabutilamonijevega bromida.