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Influence of antioxidant and neutralization on stability of historical document models with iron-gall inks

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Abstract

This work is concerned with retardation of the degradation of historical documents written in iron-gall ink. The main objective was to examine the effect of MMMC (methoxy magnesium methyl carbonate) neutralization agent on the stability of the paper substrate during accelerated ageing. Changes were monitored in the mechanical, chemical and optical properties of the paper caused by accelerated ageing by dry hot air (at 105^{o}C) and wet hot air (at 80^{o}C and 50% RH). Whatman paper substrate was modified with gelatine combined with aluminium sulphate. The effect of the deacidification agent used, MMMC, and of the antioxidant BHT on the inked paper substrate was determined on the basis of the results of the individual measurements.

Keywords: ageing, antioxidants, deacidification

Introduction

The cultural wealth of previous generations stored in libraries and archives is on paper. Like all materials, paper is also subject to natural ageing. The tragedy of manuscripts written using irongall inks is their corrosive action on the paper substrate. Corrosion of the substrate is manifested by penetration of the ink through its mass, diffusion of the colour into the surroundings of the letters and cracking to loss of the parts of the paper with the writing (Ďurovič 2000, Ďurovič et al. 2002, Daniels 2000).

Archives, libraries, museums and galleries throughout the world store large numbers of manuscripts and paintings written with iron-gall inks that are subject to a continuous process of degradation. The chemical nature of the ink is very important from the standpoint of conservation and it is not possible to resolve the problems associated with degradation in the absence of an understanding of its nature.

Corrosion of iron-gall inks occurs as a consequence of their composition and is represented by two main degradation processes. On the one hand, this consists in the hydrolytic degradation of the paper substrate catalyzed by acids that are added to the inks during their preparation or released by a chemical reaction during the formation of the coloured components of the ink.

The second mechanism of degradation of the paper substrate consists in oxidation of the cellulose, catalyzed by the transition metals contained in iron-gall inks. Because of the presence of reducing substances, these inks contain ferrous ions even after centuries (Havlinova et al. 2007, Daniels 2000, Remazeilles et al. 2004, Krekel 1999, Rouchon-Quillet et al. 2004).

Climatic conditions, and also the manner of storing the documents, constitute another important factor affecting the degradation of the paper. The lifetimes of paper documents can be prolonged by various preliminary interventions, such as ensuring optimal temperature and relative humidity, protection against light and dust, etc (Havlinova et al. 2009).
Accelerated artificial ageing is the most frequently employed model method for predicting the behaviour of material over a longer period of time and can thus provide information and form a basis for preventative protection and maintenance of collections in archives and libraries. It is the obligation of archives and libraries to collect, store and provide access to their funds, to take care of their optimal physical condition and to pass on our cultural heritage to future generations (Havlinova et al. 2007).

A number of deacidification methods are used throughout the world, that are based on aqueous and nonaqueous procedures, using various combinations of solvents suitable for various kinds of papers (Ďurovič 2000, Ďurovič et al. 2002).

This work was performed to determine the effect of deacidification using a methanol solution of MMMC (methoxy magnesium methyl carbonate) on the stabilization of iron-gall ink. Simultaneously, the antioxidant BHT (2,6-ditertbutyl-4-methyl phenol) was used to retard degradation. The mechanical, optical and chemical properties of model samples of inks during accelerated ageing were monitored.

Deacidification processes

Corrosion of graphic symbols written using iron-gall inks represents one of the most serious forms of damage to paper and parchment documents. As a consequence of this damage, information is lost as a result of loss of the letters and simultaneously of break-down of the writing substrate.

It is a difficult matter to decide in which way to prevent continued decomposition of the ink and substrate. Stopping the hydrolytic degradation of the cellulose chain through elimination of free acids could be one approach. A number of methods have been proposed for deacidification of paper and can also be used to deacidify documents written with iron-gall inks (Paulusová et al. 2000).

Neutralization does not completely stop degradation of the paper but substantially reduces it. An alkaline reserve is simultaneously introduced into the paper in the form of calcium and magnesium carbonate, creating a reserve for gradual neutralization of the acids being formed in the paper as a consequence of natural ageing and absorption of atmospheric sulphur and nitrogen oxides (Ďurovič 2000, Turanová et al. 2004).

Deacidification processes can be classified according to the medium in which the neutralization is performed, into aqueous and nonaqueous processes. The deacidification agent is an important criterion in the selection of a suitable deacidification process. Suitable deacidification agents have been investigated since the beginning of the 20th century. The first patent is dated 1936 and initiated research in this area. The problem of rapid degradation of acidic paper and documents was gradually identified in 1900 – 1949. The first work in the area of deacidification was begun in the 20th century (Ďurovič 2000, Havlínová et al. 2008). At the beginning of the 1970's, R.D. Smith developed a method for neutralization using a methanol solution of magnesium methanolate. Magnesium methanolate is a substance that is very sensitive to water, in which it hydrolyzes, reducing its neutralization effect. Consequently, G.B. Kelly soon eliminated this drawback by converting magnesium methanolate to the less sensitive carbonate MMMC (methoxy magnesium methyl carbonate). This process is internationally known as the Wei T'O process. A prototype of the equipment for mass deacidification was installed in the Canadian Public Archives in 1981. A modified Wei T'O method was introduced in the French Bibliotheque Nationale ((Ďurovič 2000, Ďurovič et al. 2002)

Methoxy magnesium methyl carbonate

MMMC is a substance that is suitable for deacidification of highly damaged manuscripts and has the great advantage that it does not wash the iron-gall ink out of the substrate and thus fixation of the ink is not required prior to its application. MMMC is an organo-metal compound, used as a deacidification agent in the Wei T'O method of nonaqueous deacidification of books. This alkoxide is soluble in organic solvents. In this form, the magnesium can be inserted into the structure of the paper from liquefied gas using a nonaqueous system (Ďurovič et al. 2002).

Chemical formula of MMMC:

$$CH_3O\text{-}Mg\text{-}O\text{-}CO\text{-}OCH_3 \ x \ CO_2$$

where **x** depends on the solvent and the temperature.
The neutralization begins with the reaction of the deacidification agent MMMC with humidity in the paper:

$$CH_3O\text{-}Mg\text{-}O\text{-}CO\text{-}O\text{-}CH_3 + 2H_2O \rightarrow Mg(OH)_2 + 2CH_3OH + CO_2 \qquad (1)$$

Other reactions also occur, with formation of $Mg(OH)_2$, $MgCO_3$ a MgO, which react with acids and form neutral salts.
For example:

$$Mg(OH)_2 + H_2SO_4 \rightarrow MgSO_4 + 2H_2O \qquad (2)$$

$$MgCO_3 + H_2SO_4 \rightarrow MgSO_4 + H_2CO_3 \qquad (3)$$

$$MgO + H_2SO_4 \rightarrow MgSO_4 + H_2O \qquad (4)$$

Over time, the magnesium oxide, magnesium hydroxide and magnesium carbonate absorb humidity and CO_2 from the air and gradually form basic magnesium carbonate ($MgO \cdot Mg(OH)_2 \cdot MgCO_3$).

$$Mg(OH)_2 + 2MgCO_3 \rightarrow MgO \cdot Mg(OH)_2 \cdot MgCO_3 + CO_2 \qquad (5)$$

Basic magnesium carbonate is stored in the fibres of the substrate and thus forms an alkaline reserve that is capable of protecting the paper against acids.

Antioxidants

Antioxidants are employed to prevent gradual degradation of the paper. In general, antioxidants can be defined as systems employed to prevent the toxic action of free acids by preventing their formation or, as soon as they are formed, by eliminating the potential consequences of their presence. Because of the importance of degradation processes in all the areas of human activity, a broad range of antioxidants is employed for various purposes, from biologically active vitamins to stabilizers of polymerization processes Havlínová et al. 2007, Strlič et al. 2005).

From a chemical standpoint, an antioxidant can be considered to be any substance that prevents oxidation of another compound by an oxidant in that it is, itself, preferentially oxidized. From a biological standpoint, it is a substance that forms nontoxic products with the reactive components at low concentrations, thus preventing oxidation of the target molecules (Strlič et al. 2005).

In this work, the antioxidant BHT (2,6-ditert-butyl-4-methylphenol) was used. BHT consists in an antioxidant based on shielded phenols. In addition to the food industry, it is also frequently employed in the cosmetic and chemical industries. BHT is well known for its association with lipids, where it acts between the lipids and the hydrophobic zone of proteins that are normally submerged in it. BHT is a white powder that can be obtained naturally as an extract from rosemary plants. It has anti-carcinogenic action, reduces the content of cholesterol and fat tissue and is safe in prescribed amounts (Havlínová et al. 2007).

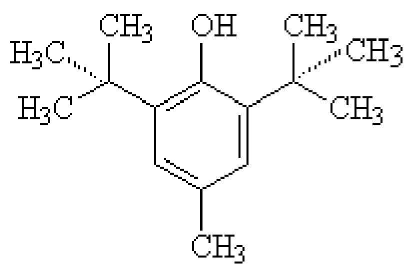

Fig. 1. Scheme of the formula of the antioxidant BHT (2 ,6-ditert-butyl-4-4-methyl phenol)

BHT is a chain-splitting antioxidant. It is a basic characteristic of these antioxidants that the newly formed aryl-oxy and amino-oxy radical does not further participate in the mechanism of the chain oxidation reaction. This is achieved by delocalization of the unpaired electrons in the aromatic ring and spherical hindrance of the group containing an unpaired, much more stable electron (Neevel 2000).

Materials and Methods

Preparation of Samples

The work was performed using high-quality Whatman No. 1 wood-free filter paper (Cat. No. 10001917), which does not contain filler, optical brightening agents and sizing agents. Samples with a size of 8x12 cm were cut out of sheets of Whatman no. 1 filter paper and were immersed for 5 minutes in a 1% solution of photo-gelatine (pH = 5-6) in combination with a 5% aqueous solution of aluminium sulphate and, after complete drainage of excess liquid, the filter paper was left to dry to constant weight at laboratory temperature. So we wonted to approximate historical paper making.

The iron-gall ink was prepared by mixing 82g tannin, 70g $FeSO_4 \cdot 7H_2O$ and 1 L of distilled water. To this mixture was added 667 ml of a solution of gum arabic (solution with a concentration of 78.5 g/L H_2O). The obtained molar ratio of iron and tannin of 5.5:1 represents the molar ratio of these basic components in preparation of inks occurring in the recipes of historical inks; the ink pH equalled 2.55.

The freshly prepared ink was applied to the samples (8x12cm) of the paper substrate by immersion for approximately 10 seconds and, after letting the excess drain off, the samples were placed between two sheets of filter paper to increase their homogeneity. Then they were left to dry at laboratory temperature and, after drying, the ink samples were left to age in a chamber for 3 hours at a temperature of 50^{o}C, as we wanted to approximate documents that had aged for some time.

The MMMC neutralization solution, prepared from a 21% methanol-solution of MMMC, diluted with methanol to a 6% solution, was further applied to the pre-aged samples. The samples were immersed in the solution for 10 seconds and placed between two sheets of filter paper.

The antioxidant BHT was prepared in two different concentrations (0.1% and 0.01% solutions in ethanol) and applied also by immersion of the sample into the neutralization solution for 10 seconds. In both cases, the samples were left to dry in the air at laboratory temperature.

Artificial Ageing and Simulation of Ink Corrosion

The first set of the sample was subjected to accelerated ageing in an OMT OVEN weathering chamber type OMT075.XX2.C (SANYO Gallenkamp, Great Britain) at a temperature of 80^{o}C and 50% RH, for a period of 1, 3, 6, 12 and 24 days.

The second set of the sample was submitted to accelerated ageing in an APT Line Series FED weathering chamber with R3.1 regulator (Fisher Scientific, s.r.o., Czech Republic) at a temperature of 105^{o}C, for a period of 1, 3, 6, 12 and 24 days.

Methods

Determination of the bending resistance was performed according to standard ISO 5626 on an Schopper (Werkstoffprufmaschinen, Leipzig, FRG) bending resistance instrument, with a spring tension of minimally 3.04 (3.09) N, maximally 3.97 N, test rate of 104 double bends per minute (angle of 180^o). The results of measurement of the mechanical properties were processed statistically. The arithmetic mean, standard deviation and reliability interval were calculated for a significance level of $\alpha = 0.05$.

The pH of an aqueous cold extract was determined according to STN ISO 6588 standard using a JENWAY model 370 (Monokrysaly Turnov, Czech Republic) digital pH meter with a precision of 0.01 pH units.

The total colour difference was determined using a Spectro-Densitometra SpectroDens TECHKON instrument from the Diatech company, with standard lighting of D50, 2^o standard colorimetric observer, measuring the absolute value. Fourier transform infrared (FTIR) spectra were measured using an EXCALIBUR, FTS 3000 MX (DIGILAB, USA) spectrophotometer, by the transmission method using KBr pellets.

Abbreviations

W+Ge – Whatman modified gelatine with aluminium sulphate

I – application of iron-gall ink

M – treatment with methoxy magnesium methyl carbonate

BHT – treatment with the antioxidant 2,6-ditertbutyl-4-methyl phenol

Results and Discussion

Mechanical properties of the prepared samples

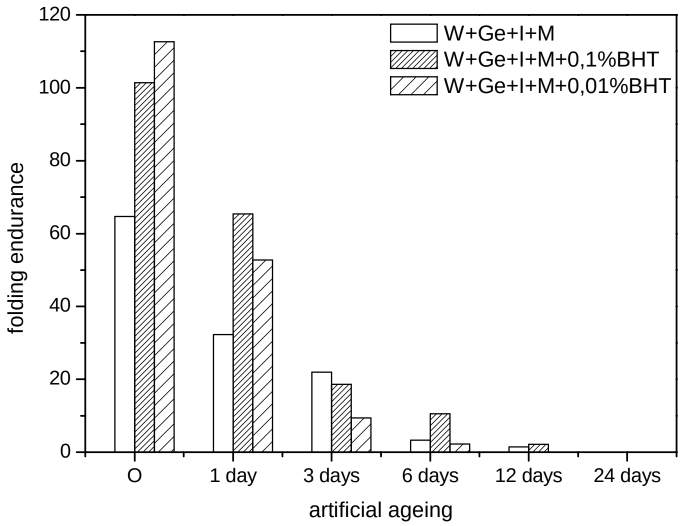

Fig. 2. Dependence of the number of folding endurance on the ageing time for wet ageing at $80^{o}C$, 50% RH for ink samples

It is apparent from table 1 that, following neutralization of the ink samples with an MMMC solution, the number of double bends increased compared to the samples without neutralization from a value of 0 to 65; however, following the third day of ageing, this value rapidly decreased. It was not possible to reduce this decrease even after application of BHT antioxidant. BHT antioxidant enabled an improvement in the mechanical properties only for unaged samples and samples aged one day. If the samples without neutralization and antioxidant (Tab. 1) are compared (i.e. only the ink paper substrate) for which there were zero values of the numbers of double bends at the beginning, these samples retained minimal mechanical properties following neutralization with MMMC and subsequent stabilization with antioxidant BHT up to twelve days of artificial ageing.

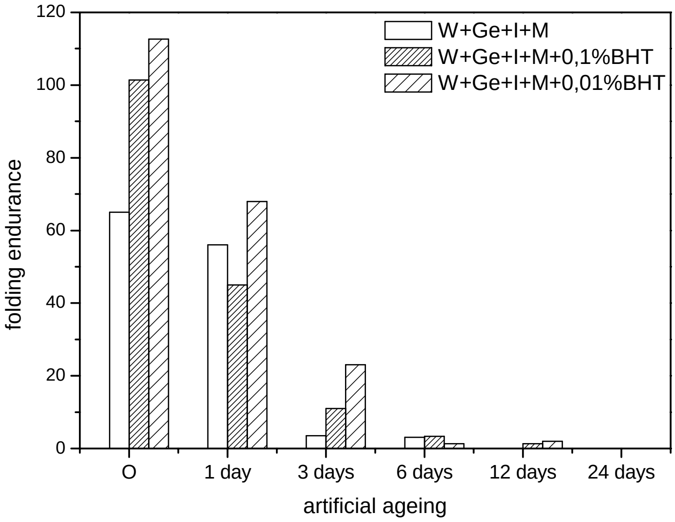

Fig. 3. Dependence of the number of folding endurance on the ageing time for dry ageing at 105^{o}C for ink samples

The ink samples exhibit low mechanical properties of the paper as a result of artificial ageing in both wet and dry heat. Deacidification of ink samples retarded the decrease in the mechanical properties (Figs. 2,3) and thus it can be assumed that the degradation of the cellulose is also retarded. The values of the numbers of double bends in Table 1 indicate that the samples aged in dry heat have lower bending resistance compared to samples aged by wet heat.

Tab. 1: Number of double bends for wet and dry ageing

Folding endurance						
Artificial ageing at 80°C, 50 % RH						
	Pre aged (3 h 50°C)	1 day	3 days	6 days	12 days	24 days
W+Ge	184±17	0	0	0	0	0
W+Ge+I	0	0	0	0	0	0
W+Ge+I+M	65±6	33±4	22±4	3,3±0,4	1,5±0,4	0
W+Ge+I+M+0,1%BHT	101±23	65±8	19±7	10,5±1,7	2,2±0,3	0
W+Ge+I+M+0,01%BHT	113±7	53±11	9,4±1	2,3±0,5	0	0
Artificial ageing at 105°C						
	Pre aged (3 h 50°C)	1 day	3 days	6 days	12 days	24 days
W+Ge	184±17	0	0	0	0	0
W+Ge+I	0	0	0	0	0	0
W+Ge+I+M	65±6	56±5	3,5±0,5	3,1±0,9	0	0
W+Ge+I+M+0,1%BHT	101±23	45±7	11±5	3,4±0,4	1,3±0,4	0
W+Ge+I+M+0,01%BHT	113±7	68±5	23±6	3,9±0,5	2±0,4	0

Determination of the pH values of the paper substrates

Following neutralization of the samples with a 6% MMMC solution (Fig. 4), the pH of the sample increased from a value of 2.88 to a value of 7.48 for unaged samples. For the ink samples, also after artificial ageing, the decrease in the pH is minimal (Fig. 4) but the decrease for the neutralized samples is up to 44% and the pH decreases down to a value of 4.16. It can be seen from Figure 4 that the pH value of the sample with BHT antioxidant decreases with increasing ageing time, from which it follows that application of the antioxidant did not stabilize the samples during the artificial ageing. Two concentrations of BHT, 0.1% and 0.01% solutions in ethanol were used, where the samples stabilized with a 0.1% BHT solution yielded somewhat higher pH values, but the differences are minimal.

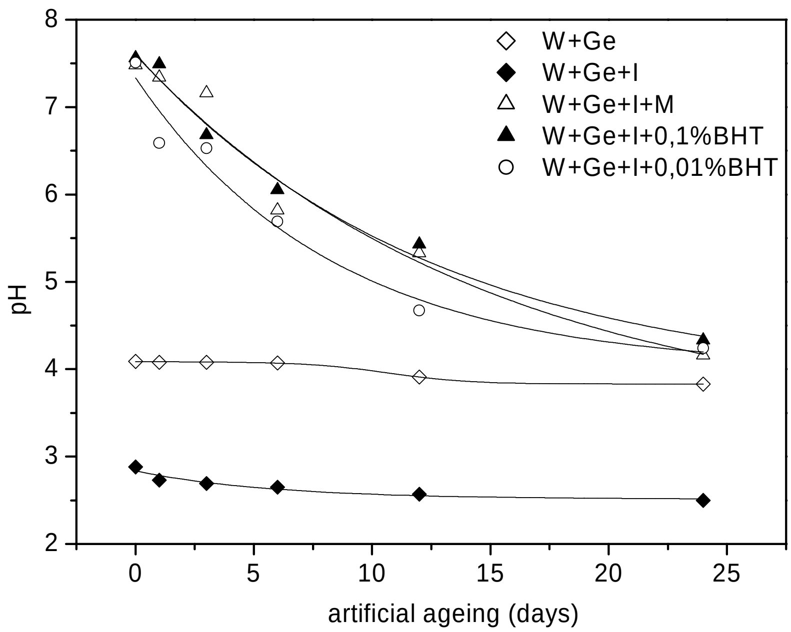

Fig. 4. Dependence of the pH on the ageing time for wet ageing at 80^{o}C, 50% RH for ink samples

A greater decrease in the pH and thus a greater increase in the acidity of the paper was observed for the wet-aged sample compared with the dry method of ageing (Fig. 4,5). In the wet ageing method, which also more closely approximated real (actual) ageing, further acids can be constantly formed and can subsequently catalyze further hydrolytic splitting of the cellulose chains.

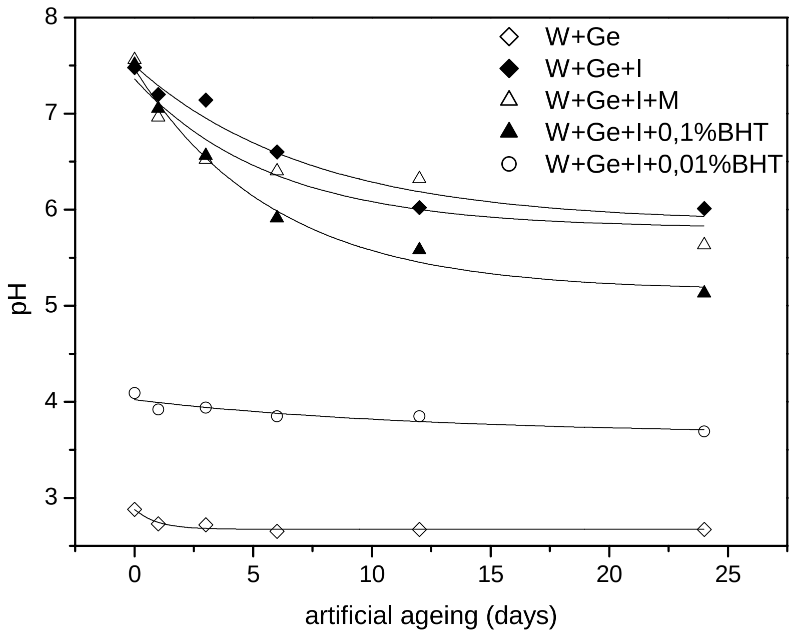

Fig. 5. Dependence of the pH on the ageing time for dry ageing at 105°C for ink samples

Optical properties of the prepared samples

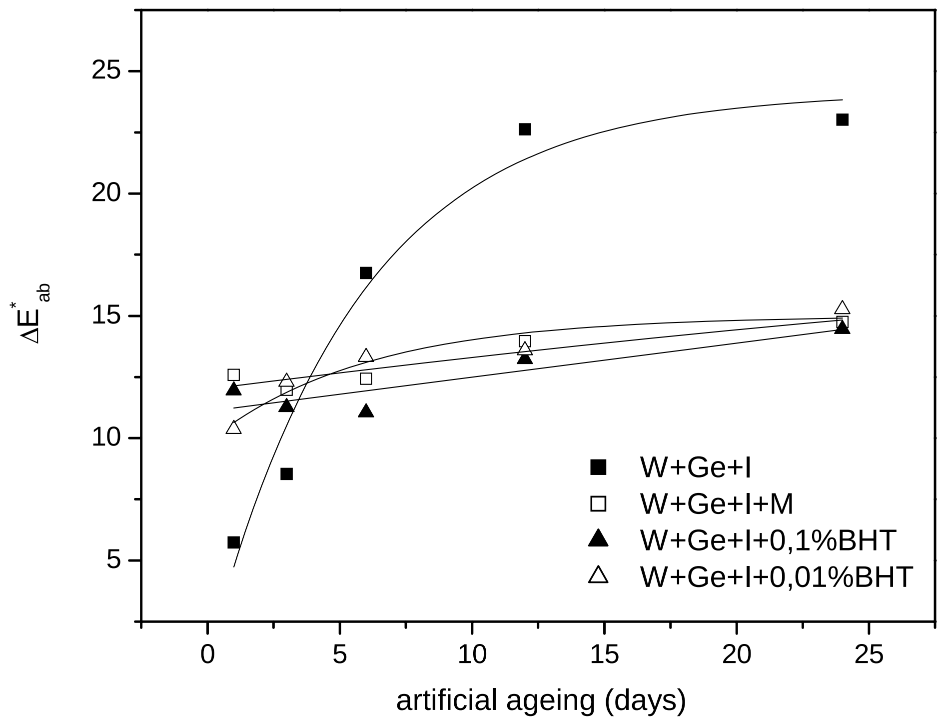

Fig. 6. Total colour difference in wet ageing at 80°C, 50% RH for samples with applied ink

It can be seen in Figure 6 that, following neutralization of the ink samples with the MMMC solution, the total colour difference vs. paper substrates before accelerated ageing increased following only a single day of ageing, from a value of 5.74 to a value of 12.59. In contrast, during ageing, MMMC reduces the value of $\mathbf{\Delta E^*_{ab}}$, where, following final ageing, i.e. 24 days, $\Delta E^*_{ab} = 14.75$, compared to the ink sample without neutralization, where the ΔE^*_{ab} value equalled up to 23.1 after final ageing.

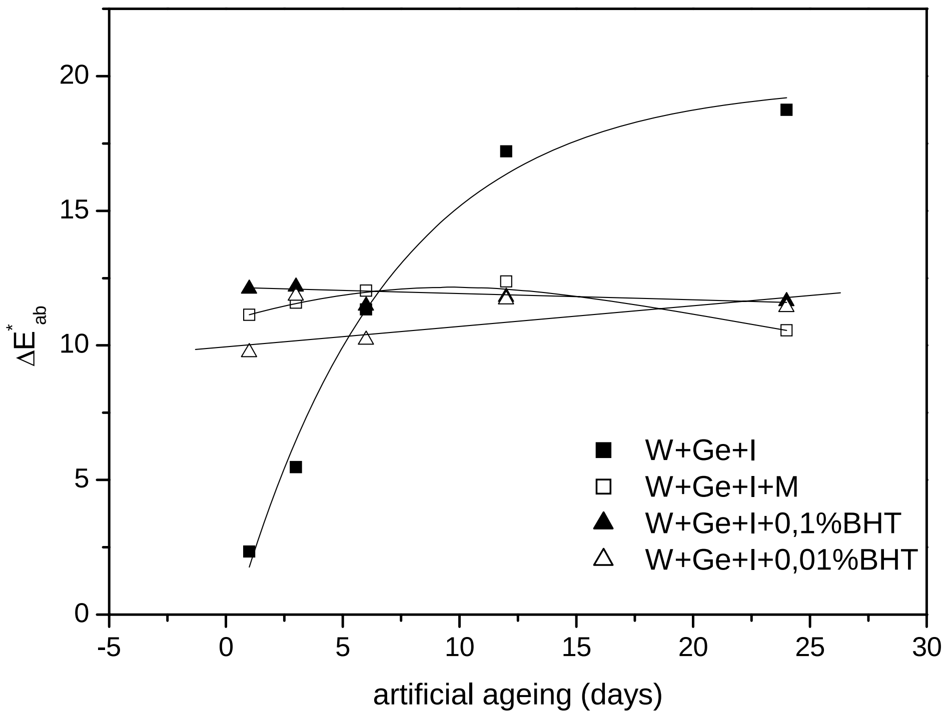

Fig. 7. Total colour difference in dry ageing at 105˚C for ink samples

In comparing the values of the total colour difference in Figures 6 and 7, it can be seen that the ink samples are more stable under the conditions of dry ageing where, for the neutralized samples, the value of $\mathbf{\Delta E^*_{ab}}$ practically did not change during artificial ageing while, in wet ageing, an increase in $\mathbf{\Delta E^*_{ab}}$ was observed.

As yellowing of the paper is accelerated by other factors than heat and humidity, such as, e.g., acidic pH of the paper, it is apparent that, for ink samples that are very acidic, an increase was observed in the value of the chromatic coordinate b*, from a value of -8.36 to a value of 13.56 (the samples acquired a yellow-brown colour). It can be seen in Figure 8 that, following neutralization of the ink samples, coordinate b* increased after one day of ageing from a value of -4.99 to a value of -2.57, but this value did not change much during ageing (the samples retained the colour of the ink).

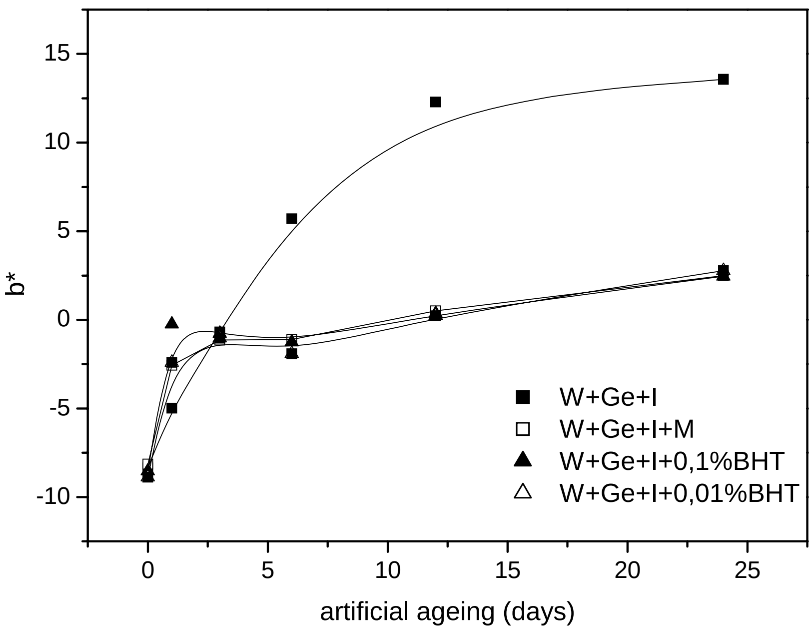

Fig. 8. The effect of accelerated wet ageing at 80^{o}C, 50% RH on the change in the chromatic coordinate b* for the ink samples

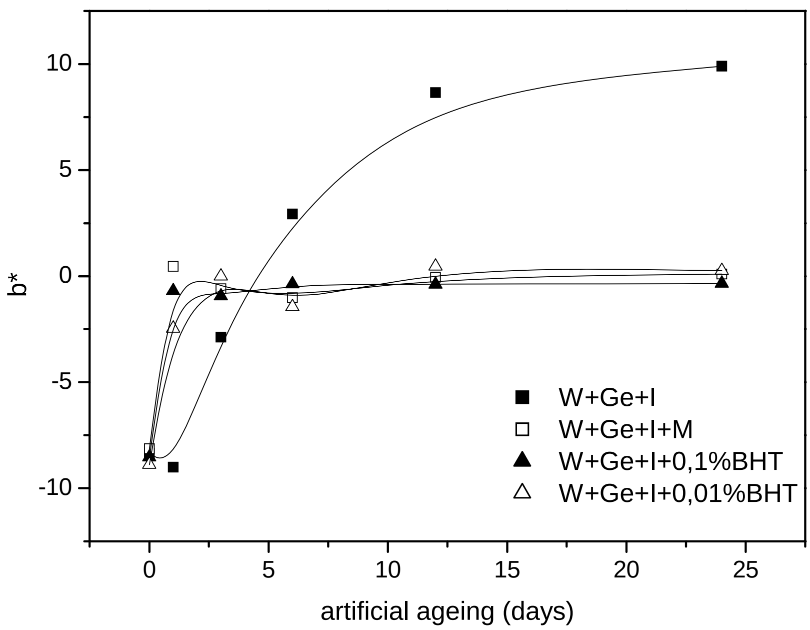

Fig. 9. The effect of accelerated dry ageing at 105^{o}C RH on the change in the chromatic coordinate b* for samples with applied ink

It can be seen from Figure 8 and 9 that wet ageing has a greater effect on the change in the chromatic coordinate b* compared with the dry ageing method, although it should be emphasized that neutralization of the ink sample using MMMC assisted in preserving the ink colour in both the wet and dry ageing methods.

Identification of chemical changes using infrared spectroscopy

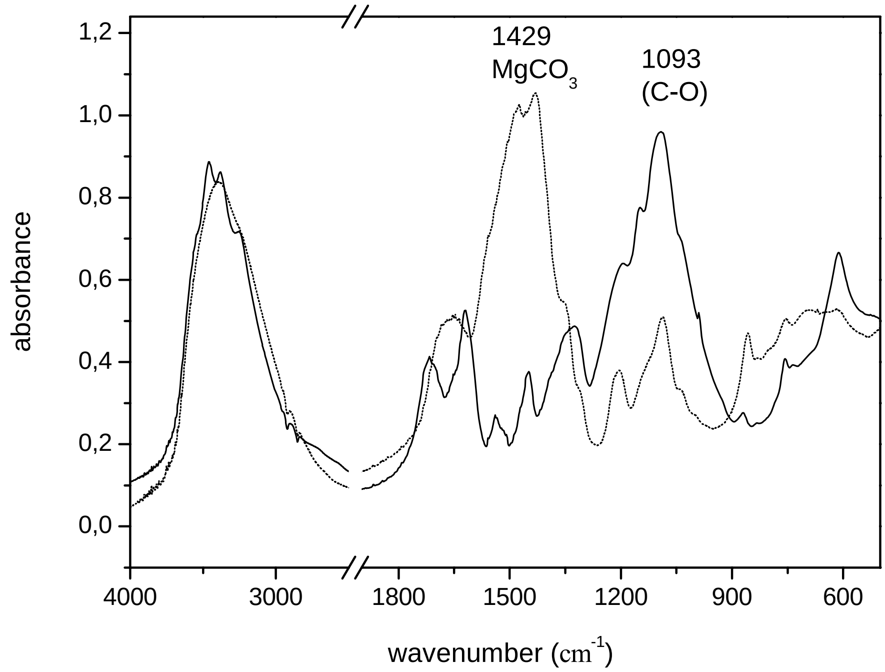

Fig. 10. FTIR spectra of iron gall ink (black line) and iron gall ink with MMMK (dot line) in pellet.

Figure 10 depicts a comparison of the FTIR spectrum of unaged ink with the spectrum of unaged neutralized ink measured in a pellet. Neutralization of the ink with a 60% MMMC solution led to a reduction of the band at 1093 cm^{-1}, which is characteristic for the C-O bond. A further change following neutralization of the ink consists in the formation of a new band in the 1429 cm^{-1} region, corresponding to the vibrations of magnesium carbonate.

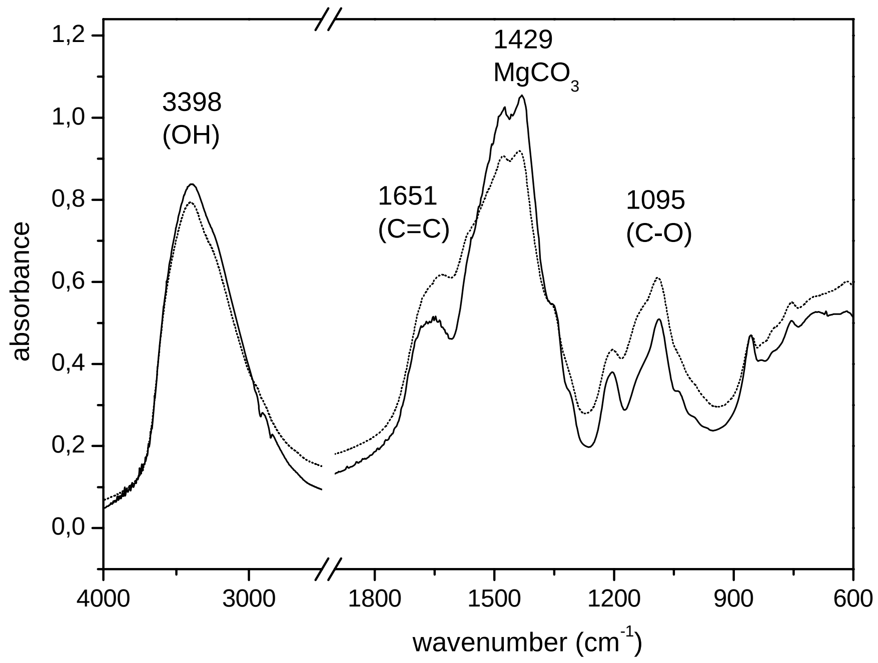

Fig. 11. FTIR spectra of iron gall ink with MMMK in pellet. Black line: no ageing, dot line: aged 3 days

Magnesium carbonate forms an alkaline reserve in the deacidified paper and, because the alkaline reserve is important for stabilization of the paper substrate, the band of magnesium carbonate was monitored during the ageing. It can be seen in Figure 11 that the band responsible for the vibrations of magnesium carbonate (1429 cm^{-1}) is already reduced after 3 days of ageing.

It is apparent from the FTIR spectra depicted in Figure 12 that this band (1429 cm^{-1}) disappears after 12 days of ageing and it can thus be assumed that the alkaline reserve was exhausted. This was also confirmed by the measured pH (Fig. 4 and Fig. 5), where the pH value of all the deacidified samples following 12 days of artificial ageing by wet and dry heat lie in the slightly acidic pH region.

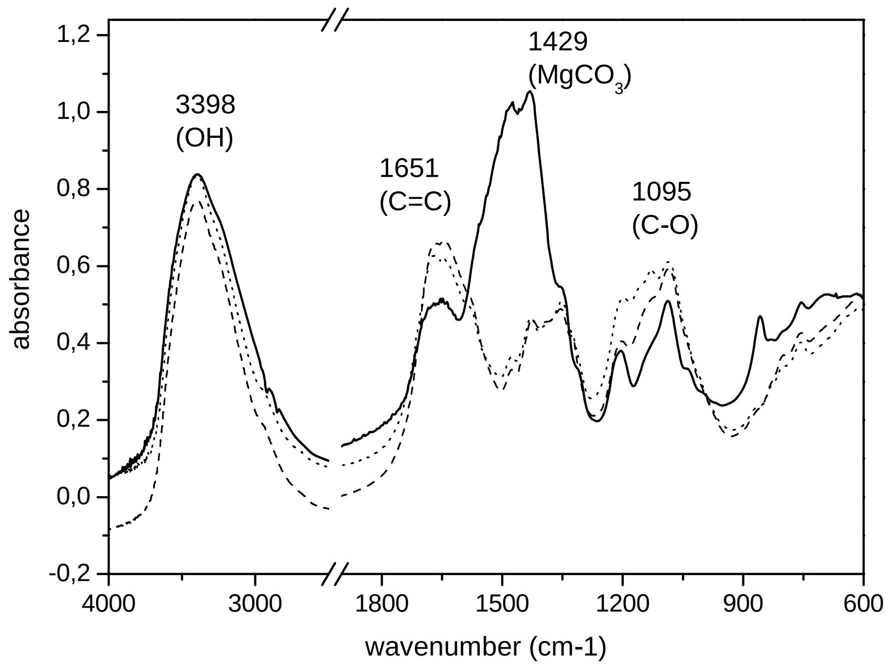

Fig. 12. FTIR spectra of iron gall ink with MMMK in pellet. Black line: no ageing, dot line: aged 12 days, dash line: aged 24 days

Conclusion

It follows from the results of the measurements that neutralization of an ink sample with a 6% methoxy magnesium methyl carbonate (MMMC) solution led to a substantial improvement in the mechanical properties, especially for unaged samples, and to an improvement in the optical and chemical properties for both unaged and aged ink samples. Measurement of the FTIR spectra confirmed that an alkaline reserve is created in the neutralized ink and thus these results indicate that neutralization of paper with an MMMC solution has a stabilizing effect. However, this alkaline reserve is exhausted after 12 days of artificial ageing. Subsequent introduction of the antioxidant 2,6-ditertbutyl-4-4-methyl phenol (BHT) into the neutralized samples improved the studied properties of the unaged paper sample; however, a stabilizing effect of the antioxidant was not demonstrated following artificial ageing.

Acknowledgement

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References

Daniels V (2000) The chemistry of Iron Gall ink. In: The Postprints of the Iron Gall Ink Meeting, Newcastle upon Tyne, University of Northumbria

Ďurovič M (2000) Hromadné odkyselovaní papírových archiválií. National Archive in Prague; Prague

Ďurovič M (2002) Restaurování a konzervování archiválií a knih. Publisher of Ladislav Horáček, Paseka, Litomyšl

Havlínová B, Mináriková J, Hanus J, Jančovičová V, Szabóová Z (2007) Restaurator 28: 112-128

Havlínová B, Maková A, Katuščák S, Čeppan M, Mikula M, Reháková M, Čepcová K (2008) Method of treating of archival paper carrier. Patent SK 286412 B6, Faculty of Chemical and Food Technology, Bratislava, ISBN PP 109-2005

Havlínová B, Katuščák S, Petrovičová M, Maková A, Brezová V (2009) Journal of Cultural Heritage 10: 222-231

Neevel JG (2000) (Im)possibilities of the phytate treatment. In: The Postprints of the Iron Gall Ink Meeting, Newcastle upon Tyne, University of Northumbria

Paulusová H, Novotná M(2000) Vliv odkyselení methoxymagnesiummethylkarbonátem na stabilitu železitogalových inkoustu. X. Seminar of restaurators and historians, Litomyšl :222-241

Krekel Ch (1999) Chemische Struktur historischer Eisengallustinten. Tintenfraßschäden und ihre Behandlung, Stuttgart

Remazeilles C, Rouchon-Quillet V, Bernard J (2004) Restaurator 25(4): 220-232;

Rouchon-Quillet V, Remazeilles C, Bernard J, Wattiaux A, Fournes L (2004) Appl.Phys.A 79: 389-392

Strlič M, Kolar J, Malešič J (2005) Stabilisation strategies, ageing and stabilisation of paper. National and University Library, Ljubljana: 181-198

Turanová M, Havlínová B, Čeppan M (2004) Deacidification of aged newsprints. In: Proceedings of the International Conference, Durability of paper and Writing, Ljubljana, Slovenia, 2004. Ed. J. Kolar, M. Strlic, J. Havermans, Ljubljana: National and University Library: 70-71