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The influence of temperature and moisture on the optical properties of cellulose in the presence of metal chlorides and glucuronic acid

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KEYWORDS: Cellulose, Glucuronic acid, Discoloration, Temperature, Calcium, Magnesium, Iron, HMF, Furfural

SUMMARY: The influence of Mg^{2+} , Ca^{2+} , Fe^{3+} ions and glucuronic acid on the dry and humid heat-induced (120–180°C) discoloration of cotton linter sheets was investigated. The quantity of the added metal ions was similar to that of metal ions found in wood and pulp.

Heat-induced ageing (120–150°C, pH 5) under dry conditions caused only slight discoloration of the reference sheets and of the sheets impregnated with the metal ions. However, during ageing at 180°C, the presence of Mg^{2+} ions accelerated the discoloration. An initial pH in the range of 3–8 had no great influence on the discoloration of the reference sheets, but a low pH in combination with Mg^{2+} ions increased the discoloration drastically. Under humid ageing conditions at 180°C (<30 min), the sheets discolored approximately twice as much as under dry conditions; the difference in discoloration caused by the metal ions was less than in dry ageing.

Adding glucuronic acid to the sheets caused extensive discoloration under dry ageing conditions (120–180°C), while Ca^{2+} and Mg^{2+} ions decreased the glucuronic acid induced discoloration. Under humid conditions (180°C), however, Mg^{2+} and Ca^{2+} ions did not prevent the discoloration caused by glucuronic acid.

An increase in the absorption coefficient was observed at 285 nm, most likely due to the formation of 5-hydroxymethyl-furfural (HMF) and 2-furaldehyde (furfural). GC-MS analysis reveals increased formation of HMF in the sheets impregnated with Mg^{2+} ions. Degradation of the cellulose in which the alkaline earth metals act as Lewis acids is proposed.

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Knowledge of the behavior of cellulose material at high temperatures is important for many industrial processes, for example, in producing mechanical and chemical pulps and in producing materials containing lignocellulose fibers. High temperatures induce chemical changes in the wood components. The changes in reflectance and light absorption in the UV region give information about the formation of potential color precursors, leucochromophores. These can undergo further reactions forming colored substances, chromophores that are detectable in the visible region (Schmidt, Heitner 1993).

Chemical pulps consist almost exclusively of cellulose and hemicelluloses. Hexenuronic acid, which is formed during kraft cooking, is more pronounced in hardwood pulps due to the higher native xylan content (Hon,

Shiraishi 2001). Some of the hexenuronic acids remain after bleaching and may cause severe brightness reversion (Granström et al. 2001; Simão et al. 2005; Sevastyanova et al. 2006). Other constituents in carbohydrates such as carbonyl groups can also cause heat-induced discoloration of the pulp (Chirat, de la Chapelle 1999). Thermal treatment causes formation of furan compounds from carbohydrates in chemical and mechanical pulps (Forssskåhl et al. 2000).

Carbohydrates are generally degraded more slowly in alkali than in acid. The main degradation pathways of cellulose in alkali are the endwise peeling reaction and alkaline hydrolysis (Hon, Shiraishi 2001). The acid hydrolysis of cellulose and hemicelluloses is a rapid reaction that increases with increasing acid strength and temperature. The acid hydrolysis of cellulose (1) initially yields glucose (2), which can form 5-hydroxymethyl-furfural (3, HMF) (Fig 1, A). The acid hydrolysis of hemicelluloses containing furanoses yields furfural. The glucuronic acid unit in xylan reduces the hydrolysis rate under either alkaline or acidic conditions (Hon, Shiraishi 2001).

The rate of oxidation of carbohydrates depends on pH, moisture, temperature, access to oxidizing agents, and the presence of transition metal ions (Williams et al. 1977; Shafizadeh, Bradbury 1979; Garves 1981; Bicchieri, Papa 1996; Kolar 1997; Hon, Shiraishi 2001; Calvini, Gorassini 2002; Selih et al. 2007). The oxidative degradation of cellulose is enhanced under alkaline conditions; the oxidation is accompanied by the formation of peroxide or peroxy radicals (Shafizadeh, Bradbury 1979; Kolar 1997; Strlic et al. 2000). Oxidized glucose units in the cellulose chain are capable of further reactions, leading to the cleavage of the cellulose chain and the formation of colored compounds (Rapson, Corbi 1964; Luetzow, Theander 1974).

Thermal degradation of cellulose (1) at low to moderate temperatures yields 5-hydroxymethyl-furfural (3, HMF), which can decompose to form 2-furaldehyde (4, furfural) (Fig 1, B) (Emsley, Stevens 1994). Furfural also can be formed via levoglucosan (5) (Fig 1, C) (Fagerson 1969; Emsley, Stevens 1994; Li et al. 2005). Water evolves via the thermal degradation of carbohydrates; therefore, a hydrolytic scission route prevails over oxidative degradation at low or moderate temperatures under dry conditions (Withmore, Bogaard 1994; Scheirs et al. 2001).

Many primary carbohydrate degradation products are colorless but undergo further reactions yielding chromophores or colored complexes with transition metals (Singh et al. 1948; Czeipel 1960; Rapson, Corbi 1964; Luetzow, Theander 1974; Popoff Theander 1972, 1976).

HMF and furfural are colorless substances. However,

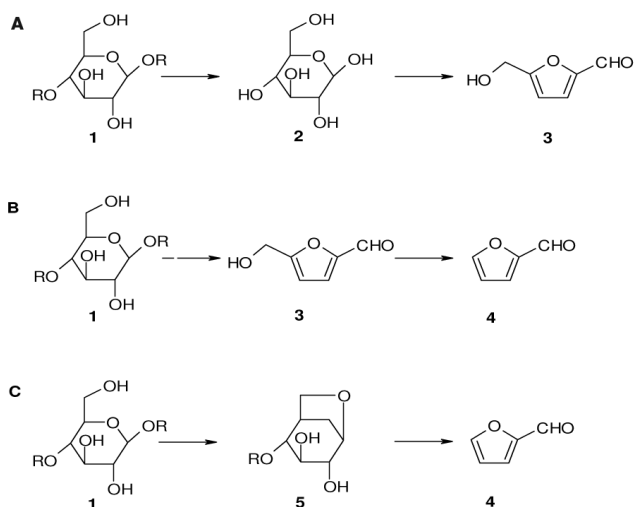


Fig 1. Different routes of cellulose (1) degradation.

A: Hydrolytic degradation: formation of 5-hydroxymethyl-furfural (HMF, 3) via glucose (2).

B: Thermal degradation: formation of HMF (3) and 2-furaldehyde (furfural, 4).

C: Thermal degradation: formation of levoglucosan (5) and furfural (4).

upon heating, HMF can cause severe discoloration (Singh et al. 1948; Forsskåhl et al. 2000) whereas furfural is more stable (Rapson, Corbi 1964).

Metal ions occur naturally in wood. Some of the most abundant metal ions in wood are sodium (10-100 ppm), manganese (10-100 ppm), iron (10-100 ppm), barium (10-100 ppm), zinc (10-100 ppm), magnesium (100-400 ppm), potassium (400-1000 ppm), and calcium (400-1000 ppm) (Stenius 2000). During the pulping processes, metal ions can be added to the pulp; these ions derive from process equipment, process water, and process chemicals (Bouchard et al. 1995; Lapierre et al. 1997; Friman et al. 2003).

Transition metal ions catalyze many chemical reactions in wood and pulp, and are therefore considered the most harmful metals in the pulping processes. Unlike transition metals, alkali, and alkaline earth metals are mostly considered beneficial or harmless to pulp and paper brightness (Czeipel 1960; Bicchieri, Papa 1996; Calvini, Gorassini 2002; Selih et al. 2007).

Lewis acids can also degrade cellulose; the metal ions form a complex with the glycosidic oxygen and the metal cation (Sarybaeva et al. 1991; Bicchieri, Papa 1996; Strlic et al. 2001).

In paper conservation, salts of alkaline earth metals are added to the paper to prevent discoloration caused by ageing. The effects of such treatments can be evaluated by accelerated ageing tests at high temperatures. The studies are mainly performed under neutral to alkaline conditions. The results of such studies are not unambiguous; some indicate that Mg^{2+} ions are a less effective stabilizer against paper discoloration and degradation than are Ca^{2+} ions, under both dry and humid ageing conditions (Williams et al. 1977; Lienardy, Van Damme 1990; Bansa 1998). Furthermore, Mg^{2+} ions can sometimes even accelerate brightness loss under accelerated ageing conditions (Kolar, Novak 1996).

Magnesium salts are sometimes added to the pulp for various reasons. Magnesium sulfate is added for stabilizing

hydrogen peroxide during bleaching, magnesium hydroxide is used instead of sodium hydroxide, and magnesium salts can also be added to avoid scaling (Colodette et al. 1989; He et al. 2004; Yu et al. 2004). It is therefore important to increase our knowledge how alkaline earth metals influences the color stability of the pulp.

In this paper, we elucidate how adding Mg^{2+} , Ca^{2+} , or Fe^{3+} ions to cellulose and adding glucuronic acid in combination with Mg^{2+} , Ca^{2+} , or Fe^{3+} ions to cellulose influences the discoloration induced by dry or humid heat ageing under slightly acidic conditions.

Materials and Methods

Cellulose and impregnation chemicals

Cotton linters with a cellulose content of 98% and a hemicellulose content of 2% were used. The pulp was essentially free of lignin and extractives. The carbohydrate composition of the cotton linter pulp after an acid wash was almost exclusively glucose (i.e., >99%).

Sodium hydroxide (NaOH, p.a.), hydrochloric acid (HCl, p.a.), ferric chloride ($FeCl_3$, p.a.), calcium chloride ($CaCl_2$, p.a.), and magnesium chloride ($MgCl_2$, p.a.) were obtained from Riel-de Haën, D-Glucuronic acid (GlcA, p.a.) was obtained from Sigma, and 5-hydroxymethyl-furfural (HMF, p.a.) were obtained from Aldrich.

Acid wash

Cotton linters were washed with HCl at pH 1.5 and 1% pulp consistency for 2 h at 18°C and thereafter five times with Milli-Q water at the same pulp consistency. During the final washing stage, the pulps were soaked in the Milli-Q water for 30 min before being dewatered. The pH of the last filtrate was neutral.

Impregnation

To compare the effects of Ca^{2+} and Mg^{2+} ions on the heat-induced discoloration of the cellulose, the molar amount of added Ca^{2+} and Mg^{2+} ions was the same (0.025 mole/kg) in the cotton linter sheets. Thus, ~600 ppm Mg^{2+} ions or ~1000 ppm Ca^{2+} ions were added to the sheets. In contrast, the molar amount of added Fe^{3+} ions was much lower (3.6×10^{-4} mole/kg), corresponding to ~20 ppm Fe^{3+} ions. The amount of added glucuronic acid was ~1.20% (w/w).

The pH of the cotton linter suspension was adjusted to the appropriate pH (3, 5, or 8) with HCl or NaOH and sheets with a grammage of approximately 30 g/m² were then produced in a laboratory sheet former.

After being dried at room temperature, the sheets were stored in a desiccator overnight before impregnation. The solutions used for impregnation were as follows: $CaCl_2$ (0.013 M), $FeCl_3$ (5.2×10^{-5} M) or $MgCl_2$ (0.012 M); or glucuronic acid (GlcA, 0.025 M); or glucuronic acid (0.025 M) with added $FeCl_3$ (3.8×10^{-5} M), $CaCl_2$ (0.013 M), or $MgCl_2$ (0.012 M); or HMF (0.025 M); or HMF (0.025 M) with added $FeCl_3$ (3.8×10^{-5} M), $CaCl_2$ (0.013 M), or $MgCl_2$ (0.012 M).

The solutions were adjusted to the appropriate pH using hydrochloric acid or sodium hydroxide in order to obtain the same initial pH. The sheets were placed on a clean polyethylene film; 3 mL of the impregnation solution were added to the sheets, which contained ~0.285 g cellulose material. After 15 min, the excess solution was removed by absorbing with blotting paper. The sheets were attached to the polyethylene film with adhesive tape and left to dry for 3 h, after which they were placed in a desiccator overnight. Square sheets were cut from the laboratory sheets and the grammage was determined before the UV-VIS reflectance spectra were recorded.

Analysis of metal content of the sheets

The cotton linter reference sheets and the impregnated cotton linter sheets were analyzed for metals using ICP-OES according to the procedure described in Friman et al. (2003).

Analysis of glucuronic acid content

The glucuronic acid content was analyzed according to Taylor and Buchanan-Smith (1992), with some modification.

First, 0.1 g samples of cellulose containing known amounts of glucuronic acid were prepared and treated according to the method for obtaining a calibration curve. A reference sample of untreated cellulose was also prepared.

Then, 0.1 g of glucuronic acid-impregnated sheet was heated with 2 mL of water in a sealed silica glass tube for 2 h, after which 0.5 mL of the water extract was removed for analysis.

To the water extracts, 3 mL of a sulfuric acid solution (80%) containing $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$ (0.80 g/L) was added, along with 100 μL of Carbazole in 95% ethanol. The tubes were carefully mixed and put in a water bath at 60°C for 2 h. The solutions were analyzed using a Cary 100 Bio UV-Vis spectrophotometer (Varian, Palo Alto, CA) at 530 nm.

pH measurements

The measurements were made according to SCAN-P 14:65, except that a solution of NaCl (100 mM) was used instead of water.

GC-MS analysis

To analyze the degradation products of the aged cellulose samples, 100 or 200 mg of the cellulose sample was put into a glass vial and heated to 60°C for 15 minutes. A headspace syringe (SPME) was used to adsorb the volatile substances. The analyses were carried out on a gas chromatograph that was connected to a single quadrupole mass spectrometer (Thermos, model DSQ). A Varian VF-5ms GC-column (30 m., 0.25 mm I.D., 0.25 μm film thickness) was used to separate the substances. The helium carrier gas flow rate was 1.0 ml/min. The injector temperature was set at 230°C and the GC temperature program was as follows: 40°C (1 min) - 20°C/min - 240°C (5 min).

Relevant peaks were identified by MS by using electron impact (70 eV) as ionization mode. The

molecular ions of 5-hydroxymethyl-furfural ($m/z = 126$) and 2-furaldehyde ($m/z = 96$), which are two of several degradation products, were identified.

Determining s- and k-values

The reflectance spectra of the sheets were recorded using a Varian Cary 100 Bio UV-Vis spectrophotometer with a 70-mm-diameter integrating sphere coated with Spectralon®. The reflectance spectra were recorded in the 250–700 nm wavelength range. The two-background method (Schmidt, Heitner 1993; Pauler 2002) was used, and calculations using the Kubelka-Munk equations yielded the light scattering coefficient, s (m^2/kg), and light absorption coefficient, k (m^2/kg). Although the grammage of the sheets was quite high (30 g/m^2), the calculated s -values decreased smoothly from 250-700 nm in the figures presented here, so the sometimes high k -values were correctly determined.

Heat-induced ageing of samples

Reference cotton linter sheets and cotton linter sheets impregnated with Ca^{2+} , Mg^{2+} , or Fe^{3+} ions or with glucuronic acid and Ca^{2+} , Mg^{2+} , or Fe^{3+} ions were aged in a laboratory oven under dry conditions at 120, 150, or 180°C for 2.5, 5, 10, 30, 60, 90, 150, and 210 min. Reference sheets and sheets impregnated with Mg^{2+} ions or 1.20% glucuronic acid with a pH 3 and 8 were aged at 180°C under dry conditions and for the same periods as described above.

Reference cotton linter sheets and cotton linter sheets impregnated with Ca^{2+} , Mg^{2+} , or Fe^{3+} ions or with glucuronic acid and Ca^{2+} , Mg^{2+} , or Fe^{3+} ions were also aged under humid conditions (pH 5). The ageing experiments were performed in a chamber pressurized with steam at 180°C for 5, 10, and 30 min. The sheets were placed in a desiccator to dry overnight before the reflectance spectra were recorded and the light scattering coefficients and light absorption coefficients were determined.

Results and Discussion

To compare the effects of Ca^{2+} and Mg^{2+} ions on the heat-induced discoloration of the cellulose, the molar amount of added Ca^{2+} and Mg^{2+} ions was the same (0.025 mole/kg). The molar amount of added Fe^{3+} ions was much lower (3.5×10^{-4} mole/kg), because the iron content of wood is much lower. Thus, approximately 600 ppm Mg^{2+}

Table 1. Amounts of Ca^{2+} , Mg^{2+} , Fe^{3+} ions and glucuronic acid (GlcA) in the sheets.a

Sample	GlcA (%)	Fe^{3+} (ppm)	Ca^{2+} (ppm)	Mg^{2+} (ppm)
Reference		4 ± 0.6	12 ± 3.3	1 ± 0.3
CaCl_2		8 ± 1.5	905 ± 30	3 ± 1.3
FeCl_3		20 ± 1.8	22 ± 3.5	4 ± 0.6
MgCl_2		8 ± 1.9	20 ± 5.9	600 ± 24
GlcA	1.24 ± 0.04	6 ± 1.0	12 ± 7.5	4 ± 3
GlcA CaCl_2	1.19 ± 0.04	8 ± 1.0	995 ± 50	63 ± 2
GlcA FeCl_3	1.18 ± 0.04	24 ± 1.0	24 ± 1.0	4 ± 1
GlcA MgCl_2	1.24 ± 0.04	9 ± 1.0	20 ± 11	600 ± 50

ions, 1000 ppm Ca^{2+} ions, or 20 ppm Fe^{3+} ions was added to the cellulose sheets as shown in *Table I*.

The unaged sheets impregnated with Ca^{2+} and Mg^{2+} ions or with glucuronic acid in combination with Ca^{2+} and Mg^{2+} ions displayed no significant increase in light absorption compared to that of the reference sheets. Adding Fe^{3+} ions or glucuronic acid in combination with Fe^{3+} ions to the sheets had a slight impact on the light absorption of the unaged sheets. Iron oxides or the formation of complexes between the iron ions and the glucuronic acid probably caused the increased light absorption.

The sheets were subjected to dry ageing at 120, 150, and 180°C and humid ageing at 180°C for different periods of time. The calculated light scattering coefficients, s , decreased smoothly over the measured region (250-700 nm). This yields light absorption coefficients, k , that can be used to make a reliable comparison between the sheets before and after heat-induced ageing.

Influence of temperature and metals on the discoloration

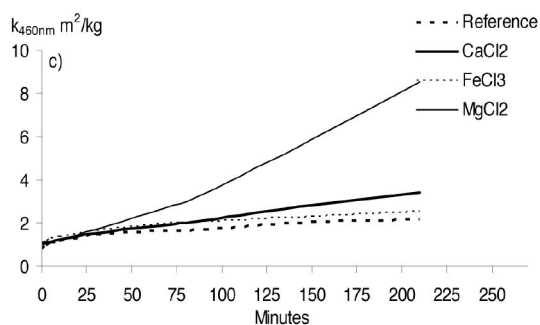
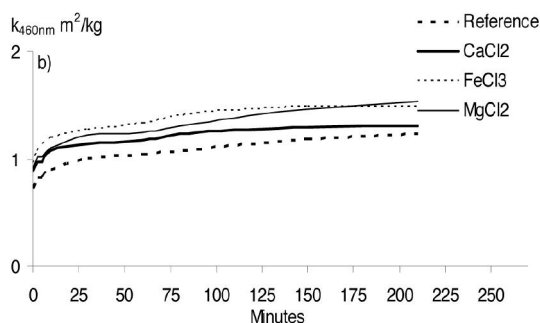
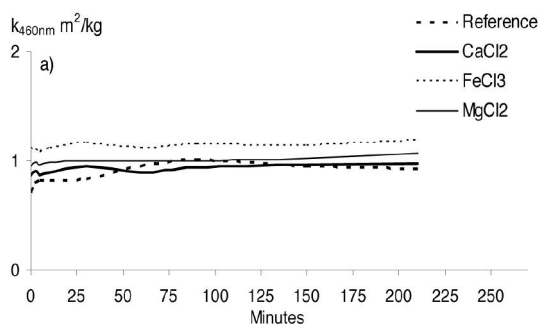
The initial pH of the sheets was 5 unless otherwise stated. The higher the temperature, the more pronounced was the ageing (*Figs 2a-c* and *3a-c*). The ageing of the

sheets was studied at 460 nm, because this is close to 457 nm, the point at which the ISO brightness is measured.

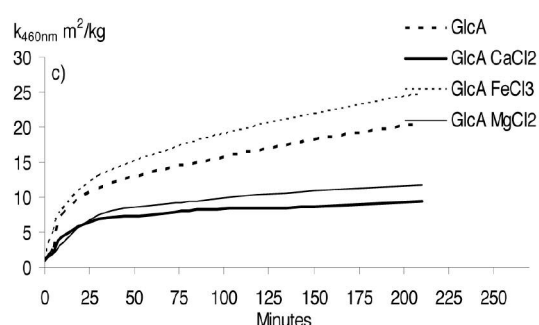
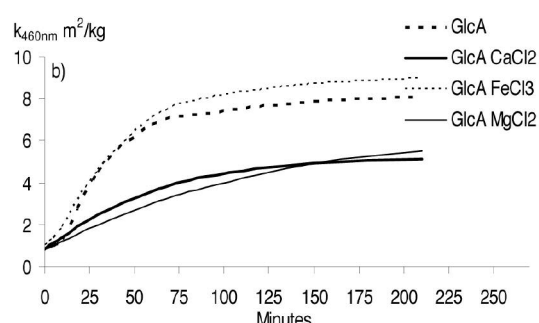
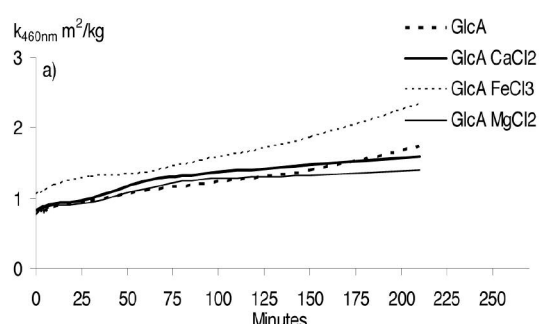
When ageing at 120°C under dry conditions, there was almost no increase in absorption at 460 nm for either the reference sheets or the sheets impregnated with metal ions. For the sheets impregnated with glucuronic acid and those impregnated with glucuronic acid and Ca^{2+} or Mg^{2+} ions, only slight discoloration was obtained (*Figs 2a* and *3a*). The sheets impregnated with glucuronic acid and Fe^{3+} ions displayed greater discoloration than did the other examined samples (*Fig 3a*).

When ageing at 150°C under dry conditions, the discoloration was more pronounced for the sheets impregnated with glucuronic acid or with glucuronic acid in combination with metal chlorides than for the reference sheets or the sheets impregnated with only metal chlorides (*Figs 2b* and *3b*).

It is evident that the samples containing glucuronic acid in combination with Ca^{2+} and Mg^{2+} ions discolored significantly less than did the sheets impregnated with glucuronic acid or with glucuronic acid in combination with Fe^{3+} ions (*Fig 3b*). Glucuronic acid discolors rapidly when heated. The slightly higher absorption in the sheets with glucuronic acid and Fe^{3+} ions is probably due to the formation of colored complexes.



Figs 2a-c. Increase in light absorption coefficient, k , at 460 nm, during ageing under dry conditions at 120, 150, and 180°C (a, b, and c, respectively) for different periods of time.



Figs 3a-c. Increase in light absorption coefficient, k , at 460 nm, during ageing under dry conditions at 120, 150, and 180°C (a, b, and c, respectively) for different periods of time.

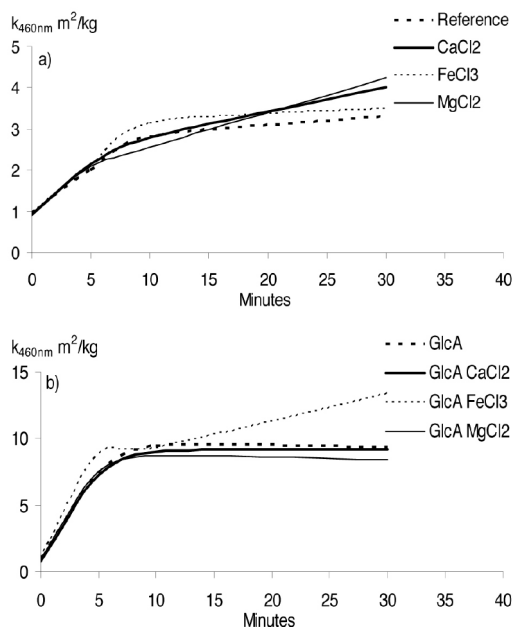
When increasing the temperature to 180°C, under dry conditions, the discoloration of all samples increased (Figs 2c and 3c). The sheets impregnated with Mg²⁺ ions displayed much greater discoloration than did the reference sheets. The discoloration of the sheets impregnated with Ca²⁺ ions was not as obvious as that of the sheets impregnated with Mg²⁺ ions, though it was somewhat greater than in the reference sheets or the sheets impregnated with Fe³⁺ ions (Fig 2c). The discoloration caused by glucuronic acid decreased when Ca²⁺ and Mg²⁺ ions were present (Fig 3c).

This indicates that under certain conditions, in this case, dry heat-ageing under slightly acidic conditions and with access to oxygen, the presence of alkaline earth metals can negatively affect the brightness stability of paper consisting mainly of cellulose.

Influence of moisture and metals on discoloration

The influence of moisture on the heat-induced ageing at 180°C was evaluated. Under humid ageing conditions, the discoloration of the sheets at 460 nm was significantly faster than under dry ageing conditions. This indicates the importance of the presence of water in chromophore-forming reactions. Under humid conditions, the metal ions have less influence on the discoloration than under dry conditions (Figs 4a and b). Humid heat-induced ageing have been reported to be less dependent on the metal ions present than in dry heat-induced ageing (Bansa 1998).

The moisture-induced discoloration at 180°C was more than twice as high as the discoloration occurring under dry conditions after 30 min, for both reference sheets and sheets impregnated with metal ions (Figs 2c and 4a). The reference sheets and the sheets impregnated with glucuronic acid and alkaline earth metal ions displayed approximately equal discoloration after 30 min (Fig 4b). Alkaline earth metal ions do not prevent discoloration caused by glucuronic acid under humid ageing



Figs 4a and b. Increase in light absorption coefficient, k , at 460 nm, during ageing under humid conditions at 180°C for different periods of time.

conditions as effectively as under dry ageing conditions. The sheets impregnated with glucuronic acid and Fe³⁺ ions became significantly discolored.

Changes in the UV region

An absorption maximum was found at 285-290 nm when ageing all samples under both dry and humid conditions. This maximum can largely be attributed to the degradation products, furfural and HMF, formed from the cellulose (Fig 5). The higher the temperature, the more pronounced the maximum and the more furfural and HMF are produced.

HMF and furfural are potential color precursors, because they can form condensed structures upon heating. Such reactions probably account for most of the observed discoloration in the visible region (Popoff, Theander 1972, 1976; Forsskähl et al. 2000).

When aged under dry and humid conditions, sheets

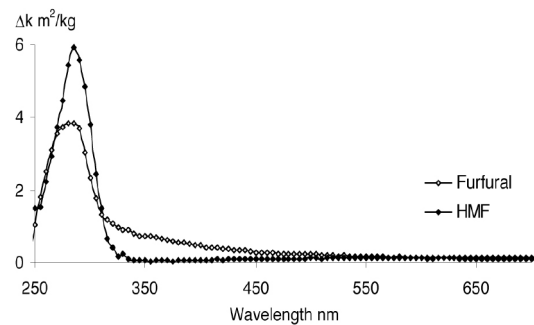
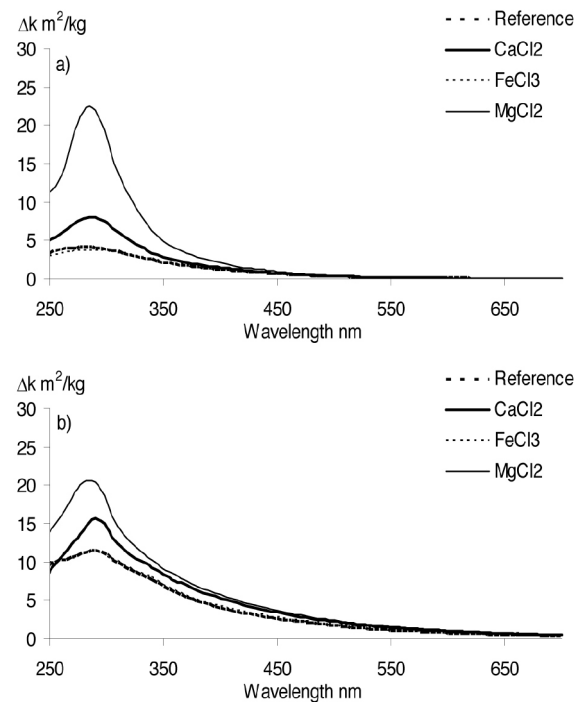
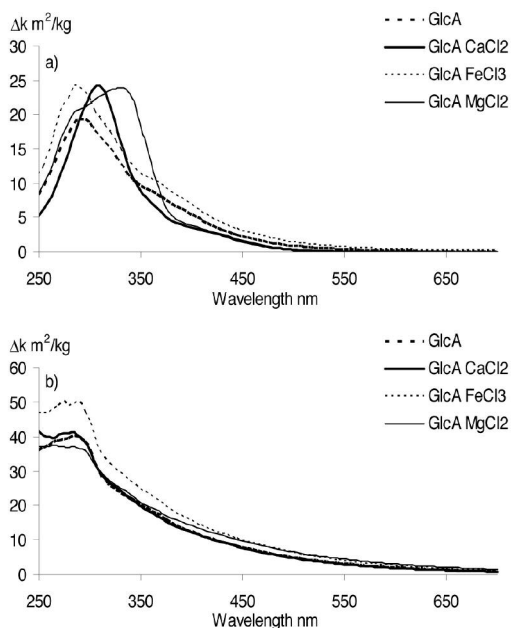


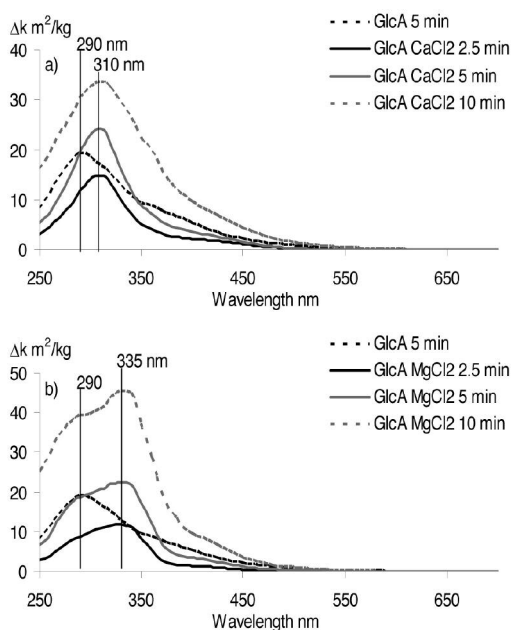
Fig 5. Δk spectra (impregnated sheet-unimpregnated sheet) of HMF and furfural. HMF has an absorption maximum at approximately 280 nm (Singh et al. 1948; Forsskähl et al. 2000).



Figs 6a and b. Δk spectra (aged sheet-unaged sheet) of cellulose impregnated with Ca²⁺, Mg²⁺, or Fe³⁺ ions aged under dry and humid conditions at 180°C for 30 minutes (a and b, respectively).



Figs 7a and b. Δk spectra (aged sheet-unaged sheet) of cellulose impregnated with glucuronic acid and with glucuronic acid in combination with Ca^{2+} , Mg^{2+} , or Fe^{3+} ions aged under dry and humid conditions at 180°C for 5 minutes (a and b, respectively).



Figs 8a and b. Δk spectra (aged sheet-unaged sheet) of cellulose impregnated with glucuronic acid and glucuronic acid in combination with Ca^{2+} (a) or Mg^{2+} (b) ions aged under dry conditions at 180°C for different periods of time.

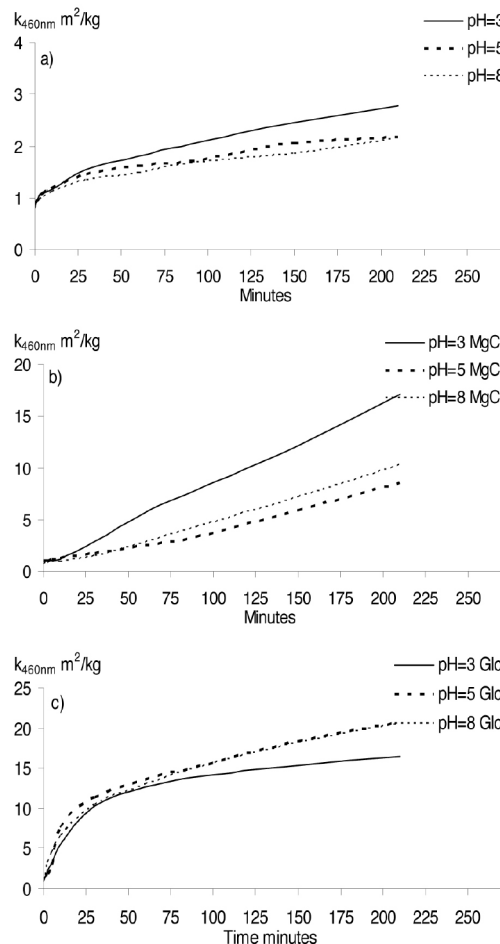
impregnated with Mg^{2+} and Ca^{2+} ions displayed spectra of similar shapes, except that sheets impregnated with Ca^{2+} ions yielded lower k -values (Figs 6a and b). This indicated that the sheets impregnated with Mg^{2+} and Ca^{2+} ions react in a similar manner.

The shapes of the spectra of the reference sheets and the sheets impregnated with Fe^{3+} ions were quite similar. One explanation is that the amounts of Fe^{3+} ions were too low to cause any significant changes in the light absorption coefficient (Figs 6a and b).

The absorption in the visible region is slightly higher for sheets impregnated with glucuronic acid or with glucuronic acid and Fe^{3+} ions than for sheets impregnated

Table 2. pH of reference sheets, metal-ion-impregnated sheets, and sheets impregnated with glucuronic acid or glucuronic acid and metal chlorides, unaged and aged under dry conditions at 180°C for 2.5 h.

Sample	Unaged samples	180°C 2.5 h
Reference	5.3	5.2
CaCl_2	5.4	5.5
FeCl_3	5.2	5.3
MgCl_2	5.4	5.3
GlcA	5.2	5.3
GlcACaCl_2	5.7	5.5
GlcAFeCl_3	5.2	5.3
GlcAMgCl_2	5.6	5.4



Figs 9a-c. Increase in light absorption coefficient, k , at 460 nm, during ageing under dry conditions at 180°C . Reference sheets, sheets impregnated with Mg^{2+} ions, and sheets impregnated with glucuronic acid (a, b, and c, respectively) at different initial pH.

with glucuronic acid and Mg^{2+} or Ca^{2+} ions when aged under dry conditions (Fig 7a). When ageing under dry conditions, the presence of Mg^{2+} or Ca^{2+} ions decreases the discoloration caused by the glucuronic acid (Fig 7a); this effect cannot be observed under humid conditions (Fig 7b). The moisture is evidently an important factor controlling the discoloration of cellulose and glucuronic acid.

For the sheets impregnated with glucuronic acid and Mg^{2+} or Ca^{2+} ions, gave rise to absorption maxima shifted towards longer wavelengths in the UV region than for sheets impregnated with only glucuronic acid when aged under dry conditions (Figs 8a and b).

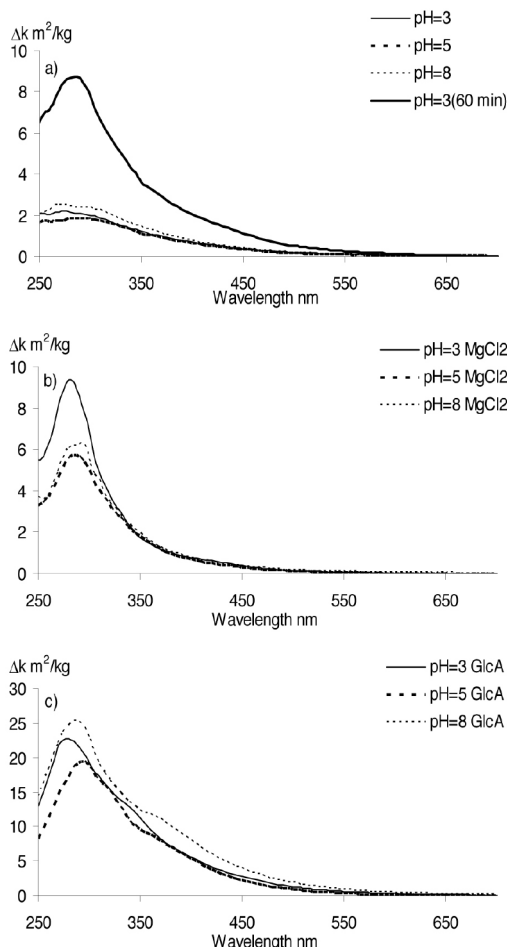


Fig 10a-c. Δk spectra (aged sheet-unaged sheet) of reference sheets, sheets impregnated with Mg^{2+} ions, and sheets impregnated with glucuronic acid (a, b, and c, respectively) at different initial pH's, aged under dry conditions at 180°C for 30 minutes.

pH measurements

To observe any change in pH accompanying the color formation, pH measurements were made on the samples. No significant change in pH was observed after 2.5 h of ageing at 180°C (see Table 2). Thus, dry heat ageing had no significant effect on the pH.

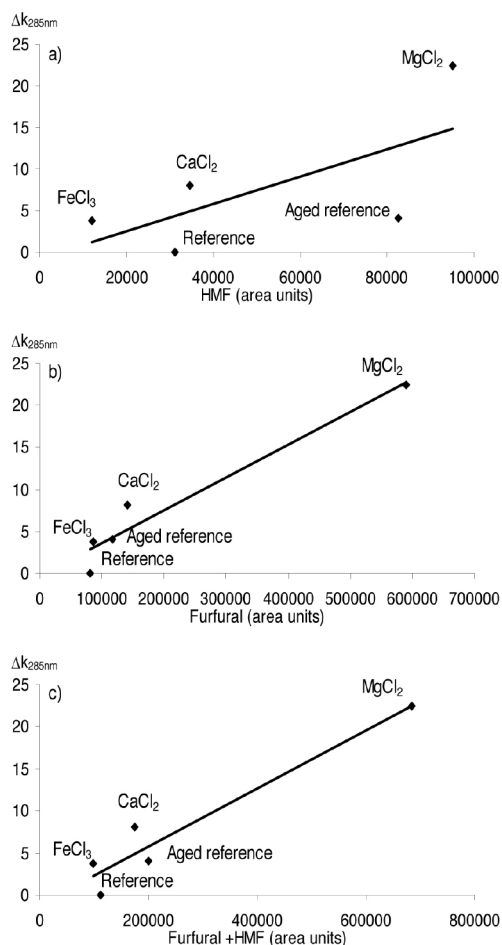
Influence of pH

In the investigations described so far, the sheets had an initial pH of 5. To evaluate the influence of pH, reference sheets were made at pH 3 and 8. Sheets impregnated with Mg^{2+} ions or glucuronic acid at pH 3 and 8 were aged under dry conditions at 180°C.

Fig 9a shows that only a small difference in the absorption at 460 nm was observed between pH 3 and 8 for the cotton linter reference sheets. However, adding Mg^{2+} ions increased the discoloration of the cotton linter sheets at all pH levels. At pH 3, the discoloration was considerable (Fig 9b). The pH had, however, a small effect on the ageing of sheets impregnated with glucuronic acid (Fig 9c).

Changes in the UV region

No pronounced absorption maximum at 285 nm was detected after 30 min for the reference sheets with an initial pH of 3 or 8, but after 60 min the absorption at 290 nm increased for sheets with an initial pH of 3 (Fig 10a). An increase in the Δk value at the adsorption maximum



Figs 11a-c. Correlation between the Δk_{285nm} of reference sheets and sheets impregnated with Ca^{2+} , Mg^{2+} , or Fe^{3+} ions aged under dry conditions at 180°C for 30 minutes and the formation of HMF, furfural and HMF + furfural, respectively.

at 285 nm was also observed in the presence of Mg^{2+} ions (Fig 10b).

Fig 10c shows the spectra of the sheets impregnated with glucuronic acid with an initial pH of 3, 5, or 8. The absorption maximum in the UV region shifts towards longer wavelengths as pH increases.

GC-MS analysis

The absorption spectra indicated increased absorption at 285 nm, which can be related to HMF and furfural formation. By plotting the change in absorption against the areas obtained using GC-MS analysis, it is possible to obtain a correlation between them. Mg^{2+} ions, which produced the highest light absorption at 285 nm, also gave rise to the most HMF and furfural (Figs 11a-c).

The amount of HMF versus Δk_{285nm} indicates that more HMF is produced when Mg^{2+} ions are present than in the aged reference (Fig 11a). The smaller amount of HMF in the sample containing Fe^{3+} ions may be due to increased decomposition of the HMF to furfural as proposed by Garves (1981). However, other degradation products may also be formed.

Fig 11b shows that addition of Ca^{2+} and Mg^{2+} ions increase the furfural formation compared to the reference. The sum of HMF and furfural versus Δk_{285nm} also correlates fairly well (Fig 11c).

Table 3. Amount (area units $\times 10^{-3}$) of HMF and furfural. (I) Reference sheets and sheets impregnated with Ca^{2+} , Mg^{2+} , or Fe^{3+} ions. (II) Sheets impregnated with HMF; or HMF with added Ca^{2+} , Mg^{2+} , or Fe^{3+} ions. All sheets (I and II) were aged under dry conditions at 180°C for 30 minutes.

Sample	HMF (I)	Furfural (I)	HMF (II)	Furfural (II)
Ref. (unaged)	31	81	n.a. ¹	n.a. ¹
Ref. (aged)	83	117	6979	305
CaCl_2	35	141	3886	351
FeCl_3	12	86	2205	142
MgCl_2	95	590	3773	789

¹ n.a. = not available

HMF or; HMF and Ca^{2+} , Mg^{2+} , or Fe^{3+} ions were added to the sheets and the sheets were aged under dry conditions at 180°C for 30 minutes (Table 3). The amount of HMF is decreased and the amount of furfural is increased if Ca^{2+} or Mg^{2+} ions are present (Table 3, II). This indicates an increased decomposition of HMF to furfural caused by alkaline metal ions. If Fe^{3+} ions are present a decrease in both HMF and furfural is displayed. This may be due to degradation of the HMF to other products such as levulinic acid (Fengel, Wegener 1989).

Several pathways lead to the formation of HMF and furfural, Fig 1. During ageing at 180°C under dry conditions, acid hydrolysis (Fig 1, A) and thermal degradation (Fig 1, B) together with oxidation of the cellulose are the most likely pathways.

Although the experiments were performed in a dry oven, the samples contained both physically and chemically absorbed water (Scheirs et al. 2001). The amount of water released during heat-induced ageing may be enough for a hydrolytic reaction to take place.

The higher amount of HMF in the samples containing Mg^{2+} ions suggests that complexes form between the cation and the glucose unit, leading to a degradation reaction promoted by the cation acting as a Lewis acid. Strlic et al. (2001) suggest the formation of complexes between alkaline earth metal ions and the glucosidic oxygen. The complexing ability of the alkaline earth metal ions correlates with the electronegativity. The formation of complexes between alkaline earth metal ions and the O-1-H and O-2-H of the glucose has also been proposed by Tajmir-Riahi (1988). Lewis-acid-promoted cleavage of the cellulose chain has been proposed by Sarybaeva et al. (1991). The increased amount of furfural in the sheets with Mg^{2+} and Ca^{2+} ions indicates that the decomposition of HMF is promoted.

It is obvious that the Mg^{2+} and Ca^{2+} ions play an important role in discoloring the cellulose material and in forming HMF and furfural.

Conclusions

Moisture is an important factor controlling the heat-induced discoloration. Adding Mg^{2+} and Ca^{2+} ions to cotton linter cellulose accelerated the heat-induced discoloration under dry conditions at 180°C , at an initial pH of 5. Adding Mg^{2+} ions increased the discoloration drastically at pH 3 compared to at pH 5 and 8. Adding Mg^{2+} and Ca^{2+} ions to cotton linter sheets impreg-

nated with glucuronic acid with an initial pH of 5 decreases the discoloration caused by the heat ageing of glucuronic acid. Under humid conditions, the positive effect of Mg^{2+} and Ca^{2+} ions on the discoloration caused by glucuronic acid was lost.

Addition of Mg^{2+} ions to the sheets increased the formation of HMF. The alkaline earth metal ions form complexes with the glucose unit. This leads to degradation of cellulose and formation of HMF. Mg^{2+} ions are suggested to act as Lewis acids. Furfural is formed in large amounts in the sheets containing Mg^{2+} and Ca^{2+} ions. If Fe^{3+} ions are present a decrease in both HMF and furfural is displayed which may be due to formation of other degradation products such as levulinic acid.

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