Use of Polycarboxylic Acid to Inhibit Heat- and Moisture- Induced Yellowing of ECF/TCF Bleached Hardwood Kraft Pulp

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ABSTRACT

The aim of this work was to inhibit the heat- and moisture- induced yellowing of ECF/TCF bleached hard wood kraft pulp (HBKP) retaining hexenuronic acid (HexA). We have already reported that one of the derivatives of HexA, 5-formyl-2-furancarboxylic acid (FFA), causes yellowing of HBKP in acidic paper, and that FFA might polymerize or react with pulp components to form new chromophoric groups (1).

In this study, it was shown that the carboxylic base of FFA interacts with that of glucuronic acid or galacturonic acid, resulting in strong yellowing. Therefore, it seems that preventing the reaction of carboxylic bases could be effective in suppressing this yellowing. We have discovered that polycarboxylic acids (for example, citric acid, tartaric acid, etc.) are useful as a yellowing inhibitor.

INTRODUCTION

Acidic paper containing aluminium sulfate is generally-used. Unfortunately, brightness reversion occurs over time. Several causes of this problem have been reported and they include oxidized carbohydrate units, hemicellulose, residual lignin, resin, metal salts or chlorinated extractives (2-5). Several environmental factors, including light, heat and moisture induce brightness reversion. In recent years, the yellowing phenomenon has become a major problem among these brightness reversions since the introduction of ECF and TCF bleaching system (1, 6-11). Yellowing often occurs in bleached hardwood kraft pulp (HBKP). Heat and moisture induce it. The difference between conventional bleached HBKP and ECF/TCF bleached HBKP is their content of hexenuronic acid (HexA). HexA tends to remain in the new bleaching system (6, 9). There is a strong relationship between the HexA content and the degree of the brightness reversion (9-11).

Yellowing can be decreased by hydrolysis of HexA, for example, by hot acid, hot chlorine dioxide or powerful ozone treatment (8, 10, 12-13). These processes have been practiced in many mills. However, pulp yield and strength loss can not be avoided. Although several yellowing inhibitors of mechanical pulp have been suggested (14-16), a compound which can suppress yellowing of ECF or TCF bleached kraft pulp has not yet been found.

Many researchers have examined and sought to explain the mechanism of yellowing. Tran indicated that carboxylic acid containing xylan and an abundance of the aldehyde and ketone might cause yellowing (17). Granström found that HexA is hydrolyzed during the ageing in paper (18), and investigated the degradation products (19). Beyer found that the color is a result of conjugated π-bonds in the furan oligomer (20). Forsskåhl also showed that a furan type compound formed in a cellulose matrix is able to cause severe yellowing after accelerated ageing with either heat or light (21). Our previous study indicated that one of the derivatives of HexA, 5-formyl-2-furancarboxylic acid (FFA), causes heat- and moisture- induced yellowing of HBKP in acidic paper, and that FFA might polymerize or react with the pulp components to form new chromophoric groups (1).

In this study, we investigated the mechanism of yellowing due to HexA and sought to identify an inhibitor.

EXPERIMENTAL

Mechanism of yellowing

Interaction of FFA with FA, neutral sugars and other pulp components

Acidic filter papers (pH3.0) were prepared by impregnating filter papers (Advantec No.2) in sulfuric acid solution (pH2.5). Acidic handsheets were made from 2g o.d. industrial bleached softwood kraft pulp (SBKP) with sulfuric acid solution (pH4.5) using a sheet machine in accordance with ISO 5269:1979. FFA, 2-furoic acid (FA), glucose, xylose and mannose were each dissolved

to 20mM with distilled water as pulp component solutions. 0.5mL of each of these solutions were then diluted to 3mL with distilled water and mixed in a plastic tray as follows: FFA, FFA+FA, FFA+Glucose, FFA+Xylose and FFA+Mannose. The filter papers and handsheets were immersed in the solutions (98 weight percent of the solution was adsorbed) and dried at room temperature. The ageing test was carried out in a humidity chamber at 80°C and 65% relative humidity for 24 hours. The b* value was measured before and after ageing. A "Yellowing Value" was determined as the difference between Δb* of the chemical added sample, Δb^*_{sample}, and Δb* of blank acidic paper, Δb^*_{blank} (Equation 1).

$$\text{Yellowing Value, } \Delta b^*_{yellowing} = \Delta b^*_{sample} - \Delta b^*_{blank} \quad (1)$$

Interaction between FFA and acidic sugars

Glucuronic acid (GlucA) and galacturonic acid (GalacA) were each dissolved to 20mM with distilled water. 0.5mL of these solutions and solution of FFA were mixed according to Table 1. Filter papers were immersed in the solutions, dried and aged as described above. The Yellowing Value was calculated using Equation 1.

Table 1 Combination of FFA and acidic sugars.

FFA
GlucA
GalacA
FFA+GlucA
FFA+GalacA
GlucA+GalacA
FFA+GlucA+GalacA

Reaction sites

The reaction sites of FFA and reactive compounds were identified using nuclear magnetic resonance (NMR). Three samples of FFA, GlucA and their compound were prepared for NMR detection as follows: (a) 2mmol each of FFA and GlucA were dissolved to 2mL of deuterium water. (b) 5mL each of 20mM FFA and GlucA solutions were mixed together, heated at 121°C for 1 hour in an autoclave and evaporated with the use of an evaporator. Deuterium water was added and then evaporated again to dryness. The remaining residue was dissolved in deuterium water.

The chemical sifts of the solutions were determined by ^1H, ^{13}C and ^{13}C-^1H two dimensional NMR spectroscopy to identify the reaction sites of FFA and GlucA. NMR spectra were detected using JEOL JNM-400spectrometer operating in the Fourier transform mode at room temperature. ^1H NMR spectra were detected at 400MHz, a π/2 pulse of 6μs, a spectral width of 8000Hz and a repetition time of 3 seconds. ^{13}C NMR spectra were detected at 100MHz, a π/2 pulse of 5μs, a spectral width of 27000Hz and a repetition time of 1.8 seconds. ^{13}C-^1H NMR spectra were detected at 100MHz and 400MHz, a π/2 pulse of 10μs and 11μs, a spectral width of 20400Hz and 4300Hz and a repetition time of 1.2 seconds.

Inhibitor of yellowing

An industrial oxygen-delignified hardwood kraft pulp of brightness 48.4%ISO, Kappa number 11.3 was bleached with the sequence D0-P-D1 to prepare a high HexA containing pulp. The pulp consistency was 10%, reaction temperature was 70°C. The reaction time and chemical charges are shown in Table 2. Handsheets were prepared with 2g o.d. laboratory-made HBKP (85.3%ISO, Kappa number 4.4), 1.2% of aluminum sulfate per o.d. pulp and sulfuric acid solution (pH4.5). 5% of low-molecular-weight carboxylic compounds (citric acid, tartaric acid, malic acid, succinate acid, glycolic acid, lactic acid, gluconic acid, malonic acid and itaconic acid) per o.d. pulp were dissolved with 3mL distilled water. The chemical charge of citric acid and tartaric acid were changed from 5% to 0.1, 0.5 and 1.0%. Polyacrylic acids whose molecular weight ranged from 5,000 to 250,000 and carboxymethyl cellulose (CMC) were used as polycarboxylic acid. The chemical charge was 0.5% per o.d. pulp.

The handsheets were immersed in each solution, dried and aged in the same way as before. b* values were measured and Δb* was calculated by b* difference before ageing and after ageing.

Table 2 Reaction time and chemical charges of each bleaching stage.

Stage	D0	P	D1
Time (min.)	40	120	120
Chemical	ClO_2	NaOH / H_2O_2	ClO_2
Charge (%)	0.35	1.0 / 0.5	0.2

Size press coating of sodium citrate

Relationship between Kappa number of pulp and charge of sodium citrate

The same high HexA containing pulp with a Kappa number of 4.4 as prepared in the above experiment was used to investigate the relationship between the Kappa number of HBKP and the optimum chemical charge of an inhibitor. The HBKP was beaten to CSF 506mL using a Niagara test beater. Handsheets were prepared from 3.75g o.d. beaten pulp, 0.5% of rosin dispersion agent, 0.55% of cationic starch, 0.8% of aluminum sulfate and 100ppm of retention aide. Starch (1.5g/m^2), surface sizing reagent (0.2g/m^2) and sodium citrate were size pressed by a laboratory size press tester. The size pressed sheets were dried by a cylinder dryer and aged. Δb* was calculated.

Paper properties

Starch, surface sizing reagent and sodium citrate were size pressed according to Table 3 on industrial no-sized paper (59.1g/m^2) using a laboratory size press tester. The size pressed sheets were dried by cylinder dryer and aged. The physical paper properties and Stöckigt sizing degree were evaluated.

Table 3 Target pickup.

	Target pickup (g/m^2)		
	Starch	Surface sizing reagent	Sodium citrate
Blank	1.50	0.20	0.00
Test1	1.50	0.20	0.25
Test2	1.50	0.20	0.50
Test3	1.50	0.35	0.50

RESULTS AND DISCUSSION

Reactive compound to FFA

Interaction of FFA with FA, neutral sugars and other pulp components

The reactive partners of FFA were researched among another HexA derivative, FA and neutral sugars. The Yellowing Values of the papers added FFA, FA and neutral sugars are shown in Fig.1. FFA produces a yellow material by itself. FA and neutral sugars do not contribute to the formation of yellow material. The effect of other pulp components was studied by the comparative investigation of filter paper and the handsheet made from the SBKP. The degree of yellowing of the SBKP handsheet is larger than that of the filter paper. This shows that other pulp components affect yellowing.

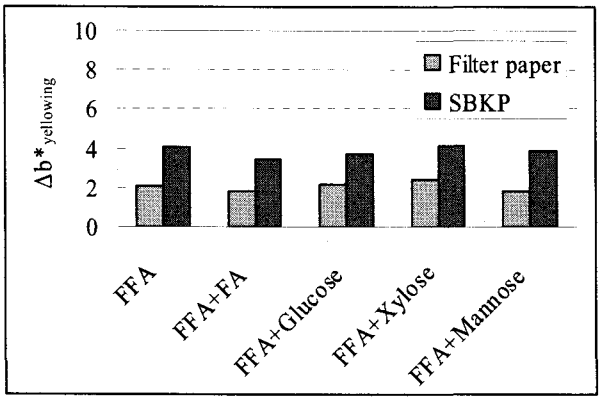

Fig.1 Interaction between FFA and neutral sugars, other pulp components.

Interaction between FFA and acidic sugars

In order to determine the reactive pulp component, the interaction between FFA and acidic sugars was studied (Fig.2). While GlucA and GalacA produce yellow material independently, the yellowing is greatly intensified when they are combined with FFA. The effect of the combination of GlucA and GalacA was also investigated. They do not work synergistically in increasing yellowing. It would seem that acidic sugars react with FFA to produce yellow material. The effect of GlucA is stronger than that of GalacA. The degree of yellowing was unchanged when GalacA was added to the mixture of FFA and GlucA.

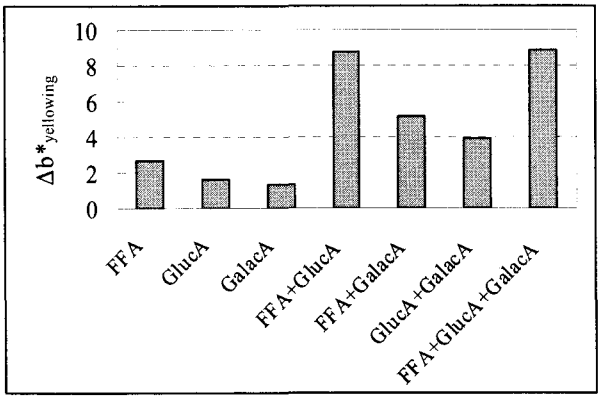

Fig.2 Interaction between FFA and acidic sugars.

Reaction sites

The carbon NMR spectra of FFA, GlucA and the resulting reacted compound are shown in Figure 3-5. The chemical shifts of C1-C4 of FFA are confirmed. The chemical sifts of C1 and C2 are larger than those of C3 and C4. It seems that carboxylic acid is a favored reaction site with GlucA. On the other hand, the spectra of GlucA reveal that carboxylic acid has a degree of reactivity, while the aldehyde group is stable. The results of these experiments illustrate the possibility that carboxylic acids of FFA and GlucA are reaction sites. It seems that yellowing can be suppressed by capping one of these functional groups. The carboxylic compound seems to react with them.

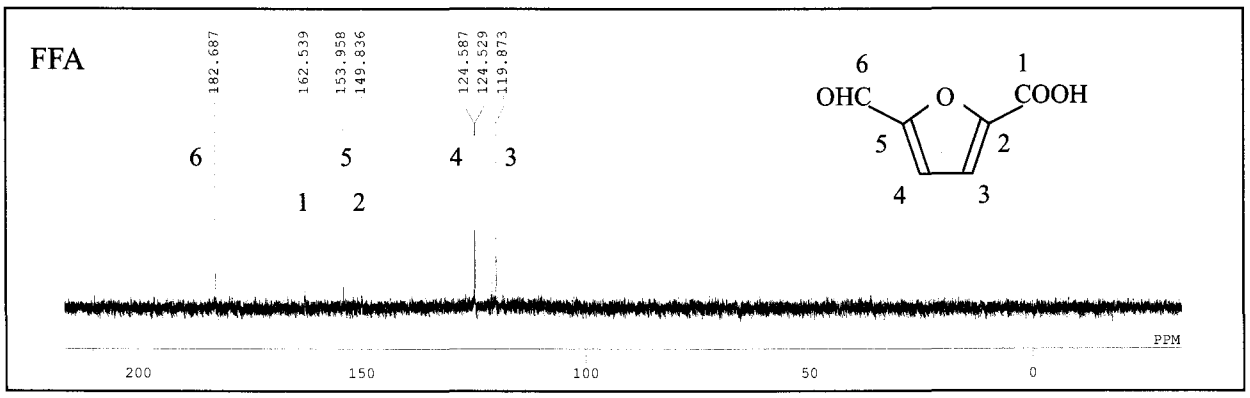

Fig.3 NMR spectra of FFA.

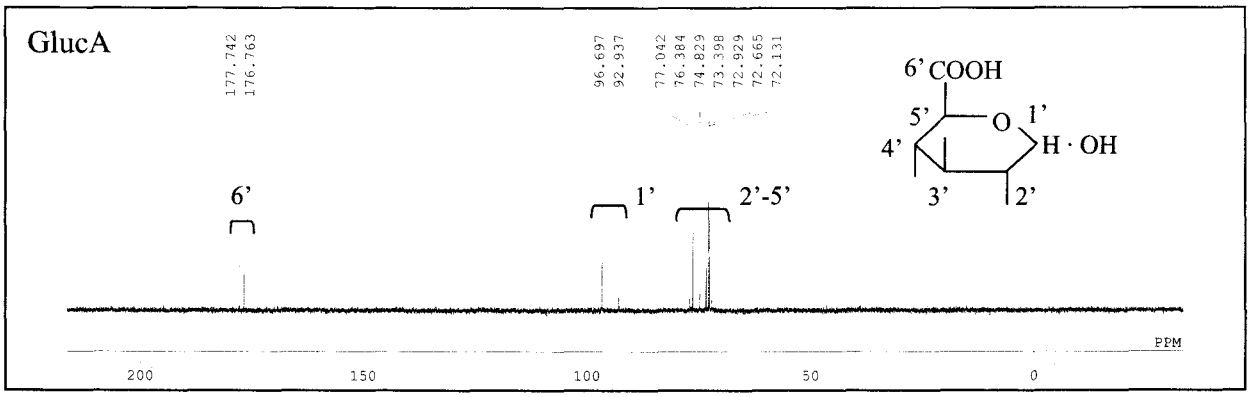

Fig.4 NMR spectra of GlucA.

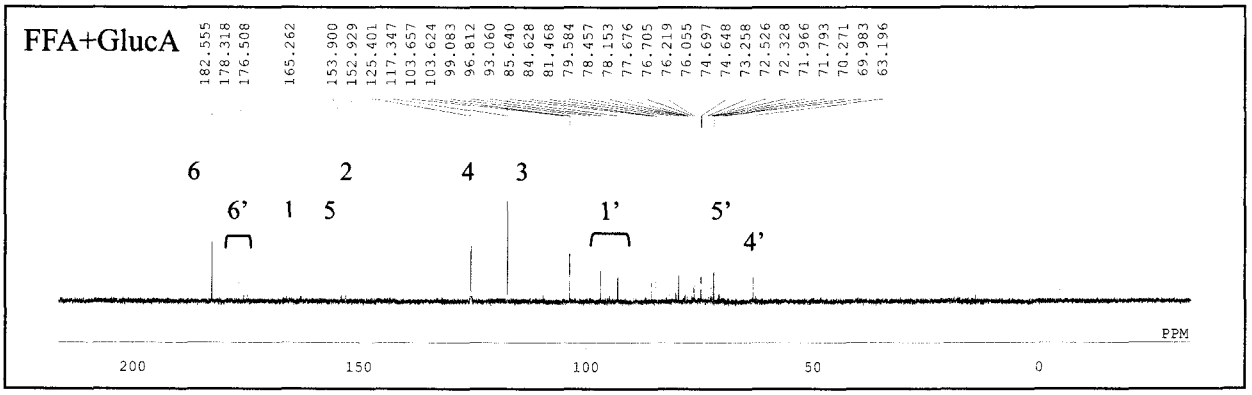

Fig.5 NMR spectra of the compound of FFA and GlucA.

Inhibitor of yellowing

The results of adding low-molecular-weight carboxylic compounds to the acidic handsheets made from high HexA containing HBKP are shown in Figure 6. Citric acid, tartaric acid, malic acid, succinate acid, gluconic acid, malonic acid and itaconic acid reduce yellowing, while glycolic acid and lactic acid have no effect. It seems that the larger the number of carboxylic groups in a molecule, the higher the reactive probability. The relationship between the charges of citric and tartaric acids with yellowing suppression indicates that it is possible to decrease yellowing effectively by adding over 0.5% of the polycarboxylic acid to the paper (Fig.7). Table 4 shows that polyacrylic acid (PAA) can also block the production of yellowing, but CMC does not work. Comparison of the effect of PAA (Table 4) and that of citric acid (Fig.7) shows that the inhibiting ability of PAA is lower than that of citric acid. This supports the idea that the number of carboxylic groups in a molecule is important.

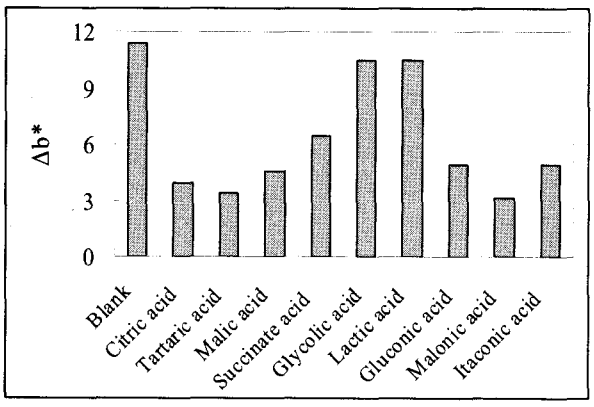

Fig.6 Effect of inhibiting yellowing by low-molecular-weight carboxylic compound.

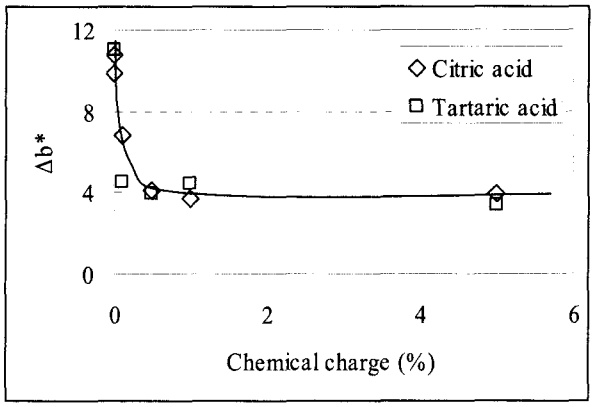

Fig.7 Relationship between chemical charge of citric acid and tartaric acid, and effect of inhibiting yellowing.

Table 4 Effect of polymers.

	Δb*
Blank	12.7
PAA (5,000*)	9.8
PAA (25,000)	9.3
PAA (250,000)	9.1
CMC	13.0

* The number in the blank is molecular-weight.

Size press coating of sodium citrate

Relationship between Kappa number of pulp and charge of sodium citrate

A size press coating test was carried out as one of the practical ways to add an inhibitor to the paper. A sufficient pickup of sodium citrate to suppress yellowing of the acidic paper made from HBKP with a Kappa number of 4.4, is 0.3g/m^2 (Fig.8).

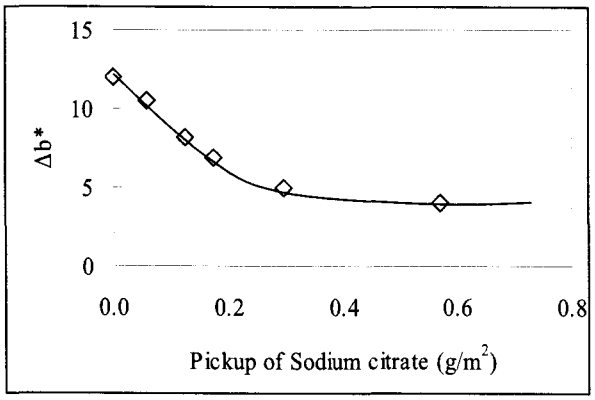

Fig.8 Relationship between yellowing and pickup of sodium citrate.

Paper properties

Table 5 shows that physical paper properties and Stöckigt sizing fastness are maintained after size press treatment with sodium citrate. The problem of ECF/ TCF bleaching is that pulp yield and strength are reduced by the hydrolysis of HexA. This study shows that such a powerful treatment could be replaced by a mild size press coating with sodium citrate.

CONCLUSIONS

HexA and acidic sugars cause heat- and moisture-induced yellowing of HBKP.

Both of their reaction sites are carboxylic acid. This indicates that it is possible to suppress yellowing by inhibiting the reaction of carboxylic acids in paper.

Low-molecular-weight carboxylic compounds (citric acid, tartaric acid, malic acid, succinic acid, gluconic acid, malonic acid and itaconic acid), polymer of carboxylic acid (PAA) and their salts can decrease yellowing.

It is possible to suppress yellowing effectively by adding over 0.5% of low-molecular-weight polycarboxylic acid to the paper.

A sufficient pickup of sodium citrate to suppress yellowing of the acidic paper made from HBKP with a Kappa number of 4.4, is 0.3g/m^2. Paper properties are maintained under this level of chemical charge.

Powerful hydrolysis can be replaced by a size press coating with sodium citrate in order to maintain pulp yield and strength. It also has the added advantages of being more environmentally-friendly and will reduce costs in the total paper making process.

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Table 5 Physical paper properties and Stöckigt sizing degree of size pressed paper with sodium citrate.

	Tear index (MD) (mN·m^2/g)	Tear index (CD) (mN·m^2/g)	Bleaking length (MD) (Km)	Bleaking length (CD) (Km)	Internal bond strength (J/m^2)	St? kigt sizing degree s()
Blank	7.9	8.8	8.5	3.5	535	28
Test1	8.8	8.8	8.1	3.6	541	29
Test2	8.5	9.5	8.2	3.5	529	27
Test3	8.3	9.2	8.4	3.5	511	26

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