The influence of process conditions during pulp storage on the optical properties of Norway spruce mechanical pulps

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KEYWORDS: High-yield pulp, Pulp storage, Process conditions, Optical properties, Colour, Spectral data

SUMMARY: The aim of this work was to study the influence of process conditions (time, pH, temperature and consistency) on the optical properties of mechanical pulps during storage in a clean system as a reference for further work. Laboratory storage trials were performed with unbleached and hydrogen-peroxide bleached well-washed Norway spruce pulps.

In general, the pulp darkened during storage due to an increase in light absorption, especially at shorter wavelengths. After long storage times, the light absorption coefficient, *k* had increased also at longer wavelengths. No specific peaks were seen in Δ*k*-spectra. The increase in light absorption was most rapid initially, during the first four hours, for all pulps when stored at high temperature (80°C), and then proceeded more slowly. The corresponding change in colour, measured as *a** and *b**, was shifted towards red and somewhat towards yellow, and over longer periods of storage, the shift towards yellow became greater. Time and temperature were found to have the largest impact. The effects were similar regardless of the starting pH (4.3-9.7) and pulp consistency (5%-25%).

The hydrogen-peroxide bleached pulps were more sensitive to storage compared to the unbleached pulp at temperatures above 50°C. At storage times of up to four hours, the unbleached pulp showed no loss of brightness at either of the storage temperatures. A slightly less bleached pulp darkened more than a highly bleached pulp at all wavelengths. The only difference measured between the two pulps was that the less bleached pulp had a higher content of iron. This higher iron content may be at least part of the reason for the more extensive darkening.

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The production of mechanical and chemimechanical pulps is an efficient way of using the available virgin fibre resources since the yield of these manufacturing processes is high and the environmental impact relatively low. The light scattering, at a given strength, and bulk properties of high-yield pulps are unique and not easily obtainable with other pulp types. In recent years the brightness (whiteness) demands for improved newsprint and magazine paper grades have been raised (Hill et al. 2010; Johnsen et al. 2010; Kuizhong et al. 2010). It is therefore important to be able to produce high-yield pulps with high brightness in environmental-friendly and cost-efficient ways.

Mill experience shows that the brightness of the bleached pulp is sometimes reduced along the process line from the bleach tower to the paper machine (Johnsen et al. 2010; Narvestad et al. 2011). The reasons for this are not easily identified and most probably vary within one mill and from one mill to the next. This is a well-known and costly phenomenon, but it is not as well documented in scientific papers as brightness reversion of the final paper sheet, an intrinsic property of mechanical pulps which has been extensively studied (see e.g. Forsskåhl 2000 and references therein; Paulsson, Parkås 2012).

In mechanical pulp, important chromophoric structures include coniferaldehydes, quinones, α-carbonyl compounds, dienone structures and iron-catechol complexes (Hon 1979; Hon, Glasser 1979; Moldenius 1983; Hon 1991; Gellerstedt 2009). Also, leucochromophores such as hydroquinones and catechol structures can, in the presence of oxygen, be converted to the corresponding quinone structures. During bleaching with hydrogen peroxide and dithionite, the chromophores react to form uncoloured groups such as hydroquinones and catechols. However, these leucochromophores may react to form coloured structures again, something that has been reported to accelerate in the presence of heavy metals (Gellerstedt, Pettersson 1980). This makes bleached pulps more susceptible to colour reversion than corresponding unbleached pulps, due to an increased possibility of quinoid structures being formed in the presence of oxygen. During storage of pulp or paper, auto-oxidation of hydroquinones and catechol groups occurs, resulting in decreased brightness especially for bleached grades (Gellerstedt 2009).

There are different opinions regarding the mechanisms for heat-induced discolouration of high-yield pulps. One is that the mechanism for heat-induced darkening is very similar to that for photo-induced darkening (Gellerstedt, Pettersson 1980; Gellerstedt et al. 1983; Gratzl 1985; Chong et al. 1991). Another opinion is that the mechanisms for heat-induced and photo-induced darkening are different and that, beside lignin, also carbohydrates most likely are involved (Polcin, Rapson 1971; Luo et al. 1988; Lee et al. 1989; Holmbom et al. 1992; Grossman, Ott 1994; Beyer et al. 1995; Fischer et al. 1995; Tylli et al. 1997; Forsskåhl et al. 2000). Transition-metal ions and especially iron have been shown to form strongly coloured complexes with lignin and extractives and therefore contribute to the darkening of mechanical-pulp sheets (Polcin, Rapson 1971; Forsskåhl 2000; Yoon et al. 1999). Both Fe^{3+} ions and Fe^{2+} ions can produce colour in pulp, either by forming complexes with phenols or by hydrolysing to form hydroxides (Gupta 1970).

Storage of unbleached and bleached softwood mechanical pulps has been reported as resulting in decreased pulp brightness (Gellerstedt et al. 1983; Harris, Karnis 1986; Lunan et al. 1986; Johnsen et al. 2010; Ferritius, Lundström 2011; Narvestad et al. 2011; Narvestad et al. 2013). Elevated temperatures in the storage tower and extended storage times are both reported to decrease pulp brightness (Harris, Karnis 1986; Johnsen et al. 2010; Narvestad et al. 2011). The influence of pulp consistency during storage of unbleached TMP was studied by Harris, Karnis (1986) and Lunan et al. (1986). In both these studies, refiner pulp was diluted with water to various consistencies, resulting in a larger decrease in brightness when the pulp was stored at a higher consistency compared to a lower consistency. In the study by Lunan et al. (1986), the brightness decrease during storage was unaffected by the pulp consistency in the range 14-50%. Storing pulp at 4% consistency did not lower the brightness at any of the temperatures evaluated, and between 4% and 14%, there was a smaller change in brightness compared to storing at higher pulp consistency. The presence of metal ions during storage was reported by Johnsen et al. (2010) as an important negative factor with regards to pulp darkening. In their study, the metal-induced darkening could be reduced or prevented using a complexing agent. This result is in agreement with the result by Gellerstedt et al. (1983) where the stability towards heat-induced ageing of a hydrogen-peroxide bleached stone groundwood pulp was improved in the presence of a complexing agent. According to Narvestad et al. (2011), the quality of the clay used in the production of SC paper is important in reducing brightness loss of bleached mechanical pulp. In a study by Narvestad et al. (2013) the clay-induced discolouration of mechanical pulp was attributed to the accessible iron in the clay. Further, control of process-water handling and the quality of dilution water was reported by Johnsen et al. 2010 and Narvestad et al. 2011 as an important factor in reducing brightness loss, where clear filtrate gave a lower brightness reduction than unfiltered water. In the study by Ferritsius and Lundström (2011), storage of unbleached SGW (stone groundwood) pulp and TMP (thermomechanical pulp) in the presence of residual hydrogen peroxide was examined. It was found that increased storage time increased the brightness of the unbleached pulp to some extent.

In a complex mill system, there are several possible mechanisms behind discolouration, such as long circulation times of components in the white water, microbiological activity, discolouration caused by paper chemicals and additives, formation of coloured groups within the dissolved and colloidal substances in the white water including metal ion complexes with lignin, lignin degradation products, or extractives, some of which will be discussed in future papers. The aim of this investigation was to study the influence of process conditions and to establish a reference for further work: the extent of darkening of well-washed unbleached and hydrogen-peroxide bleached mechanical pulps of low metal content in a clean system, measured over the visible range of wavelengths.

Materials and Methods

Materials

Pulp made from Norway spruce (*Picea abies*) was taken out on two different occasions at a SC paper mill. The first time, hydrogen-peroxide bleached pulp was collected from the wash press after a high-consistency bleach tower. The pulp consisted of 93% thermomechanical pulp (TMP) and 7% groundwood pulp. This pulp is referred to as “Bleached pulp 74.1% ISO”. The second time, unbleached pulp was taken out from the bleach press, i.e. the press before the bleach tower, and hydrogen-peroxide bleached pulp was taken out from the wash press, i.e. the press after the bleach tower. These two pulps consisted of 100% thermo-mechanical pulp and are referred to as the “Unbleached pulp” and the “Bleached pulp 71.6% ISO”. Magnesium hydroxide was used as an alkali source during hydrogen-peroxide bleaching of both bleached pulps. The unbleached pulp was taken out at a position in the mill where chelating agent had been added and was therefore comparatively clean already before the laboratory washing procedure.

The pulps were washed in two stages, before further treatment, in order to reduce the metal content. The first washing stage (Q) was performed with 2 kg/t diethylenetriaminepentaacetic acid (Dissolvine D-40-K from AkzoNobel Functional Chemicals, Amersfoort, the Netherlands) at 4% pulp consistency (p.c.) and 50°C for 30 min. The second stage (W) was performed with deionised water at 3% p.c. and 20°C for 30 min. After each washing stage, the pulp was dewatered on a wire cloth (Monodur PA 112, from Derma, Gråbo, Sweden) and the filtrate re-circulated once to avoid loss of fibre and fines. The pulp was then centrifuged to a dry content of about 35% and stored in a freezer at -24°C until further use. The metal content of the pulp was measured. Distilled water was used in all pulp washing and the laboratory trials described below.

Methods

Metal analysis

The metal content of the pulp was analyzed, after wet combustion with nitric acid using a microwave system, with an inductively coupled plasma (ICP) instrument (IRIS Advantage s/n 10973). The report limits for Ca, Cu, Fe, K, Mg, Mn and Na were 20, 0.1, 0.5, 10, 20, 0.1 and 5 mg/kg respectively.

pH adjustment

The pulp bleached to 74.1% ISO had a pH of 7.0 after 30 min when suspended in distilled water at room temperature. This pH value was therefore chosen as the midpoint in the experimental setup. The amounts of hydrochloric acid or sodium hydroxide (Merck, pro analysis) giving pH 5.0 or pH 9.0 in the pulp suspension

Table 1. Process variables evaluated for the different pulps.

	Temperature (°C)	Time (hours)	Pulp consistency (%)	pH
Unbleached pulp	50, 65, 80	1, 4, 24, 72	5	Low
Bleached pulp 71.6% ISO	50, 65, 80	1, 4, 24, 72	5	Low
Bleached pulp 74.1% ISO	50, 65, 80	1, 4, 24, 72	5, 10, 25	Low, Medium, High
Bleached pulp 74.1% ISO	60, 70	1, 4, 24, 72	5	Low

after 30 min at room temperature were chosen as low pH and high pH. The doses were optimized for each pulp.

When the storage trials were performed, the washed pulp was mixed with distilled water and stored for 15 min at room temperature prior to pH adjustment. The dose of hydrochloric acid or sodium hydroxide, determined as described above, was added to the pulp suspension. The pH after 5 min was recorded as the "starting pH".

Storage trials

The pulp storage trials were performed in a water bath according to the procedure described above. The process variables evaluated for the different pulps are described in *Table 1*.

After pH adjustment and measuring the starting pH, the pulp suspension was transferred into a polyethylene bag, and the bag was then sealed and placed in a water bath to simulate pulp tower storage. After the storage time had elapsed, the bag was placed in cold water for the pulp to cool down before sheet formation. A study by Johnsen et al. (2010) shows a good correlation between laboratory pulp storage and mill pulp storage. In their study, pulp was taken out at the inlet of the storage tower and was stored in sealed plastic bags in a water bath at 4% pulp consistency, 55°C for 3 h and 5 h at a pH 4.9-5.0. The resulting brightness was compared with the brightness at the outlet of the storage tower.

Sheet formation

Laboratory sheets with a grammage of approximately 64 g/m^2 (conditioned at 23°C and 50% relative humidity according to ISO standard method 187) were produced on a small sheet former, according to the method described by Karlsson et al. (2012). The statistical variation on sheets made from the different pulps was within the range presented in Karlsson et al. (2012). The sheet former has a 200 mesh wire with a diameter of 112 mm. Pulp sufficient for two laboratory sheets was disintegrated at 1% pulp consistency at 85°C for one minute using a Braun 300 W hand mixer with blunt mixing blades. The pulp suspension was then diluted with cold water to 0.2% pulp consistency and disintegrated for one additional minute. Sodium acetate buffer (prepared with 136.08 g $CH_3COONa*3H_2O$, 31.8 ml concentrated CH_3COOH and distilled water to one litre) was used to adjust the pH of the pulp suspension to pH 5.0 prior to sheet formation. The laboratory sheets were then pressed (5+2 min, 410 kPa over the area of the sheet), dried and conditioned at 23°C and 50% relative humidity as described in the standards ISO 5269-1 and ISO 187, respectively. Sheets with a grammage of approximately 210 g/m^2 were made to obtain an opaque background when measuring the optical properties. In this case, the pulp was disintegrated in cold water (20°C) at 3% p.c. for 30 seconds. Sodium acetate buffer (same recipe as above) was added to the pulp suspension, and the sheets were dewatered on a Büchner funnel. The sheets were then pressed for 2 min at 410 kPa, dried and conditioned at 23°C and 50% relative humidity.

Optical measurements

The measurement of optical properties was made on the top side of the laboratory sheets using a Lorentzen & Wettre Elrepho SE 070 instrument. ISO brightness, CIE L^*, a^*, b^* co-ordinates, light scattering (s) and light absorption (k) coefficients were determined according to the standard procedures ISO 2470, ISO 5631 and ISO 9416, respectively.

Results and Discussion

Some of the brightness gained during bleaching of lignin-containing pulps is frequently lost in the pulping process during transport of the pulp from the bleach tower to the paper machine (see e.g., Johnsen et al 2010; Narvestad et al. 2011). The brightness decrease can be several brightness units and represents a considerable cost for the mill (Narvestad et al. 2013). The aim of this work is to assess the influence of process conditions (time, pH, temperature and consistency) on the optical properties during pulp storage. The findings presented and discussed below were obtained in a very clean system. The effect of, for instance, metal content, process-water quality, residual process chemicals and process chemical impurities will be presented in a forthcoming paper. The conditions were chosen to resemble typical mill conditions, but also elevated temperatures and extended times were studied. The typical storage time of bleached mechanical pulp is 4-5 h, but the storage time can sometimes be longer, for example during stops in the mill. In the present study, the pulp was stored for extended times too. Smaller parts of the fibre material might end up in the white water and circulate for some time before being retained in the paper sheet. Mill experience and calculations show that the retention of wood containing fine material is low and therefore the retention time of such material can be long. In the following section, comparisons are often performed after four hours of storage, which represents relevant mill conditions. In the following figures the lines between the data points are drawn as guides to the eye, not fitted to data.

Table 2 shows some optical properties and metal contents of the well-washed softwood pulps used in the study. The unwashed pulps were comparatively clean as they were sampled at the bleach press or wash press.

However, in order to ensure that the pulps examined have a minimal content of impurities, they were washed in the laboratory as described in the experimental section. After the two-stage laboratory washing procedure, the

Table 2. Characteristics of unbleached and hydrogen-peroxide bleached pulps before and after washing.

	Unbleached pulp		Bleached pulp 71.6% ISO		Bleached pulp 74.1% ISO	
	Unwashed	Washed (Q+W)[1]	Unwashed	Washed (Q+W)[1]	Unwashed	Washed (Q+W)[1]
Brightness (% ISO)	61.9	62.4	71.1	71.6	73.9	74.1
*L**	91.0	91.1	94.3	94.6	95.5	95.3
*a**	-0.6	-0.6	-2.2	-2.3	-2.4	-2.9
*b**	14.6	14.3	12.4	12.6	12.1	11.8
k_{460} (m^2/kg)		6.4		3.0		2.4
Ca (mg/kg)	380	350	260	220	270	210
Cu (mg/kg)	0.2	0.2	0.1	0.1	<0.1	<0.1
Fe (mg/kg)	17	23	21	21	17	11
K (mg/kg)	100	60	70	60	50	30
Mg (mg/kg)	720	640	1600	1300	2000	1400
Mn (mg/kg)	7.9	0.4	5.1	0.4	2.8	0.2
Na (mg/kg)	210	130	86	86	140	64

[1]Q is wash with DTPA and W is wash with distilled water – for details see experimental section.

Table 3. pH of the pulps at the start of the storage trials.

	Unbleached pulp	Bleached pulp 71.6% ISO	Bleached pulp 74.1% ISO
High pH			9.6-9.7
Medium pH			7.1-7.2
Low pH	3.8-4.0	3.7	4.3-4.9

concentration of all measured metals was very low and the wash did not affect the optical properties of the pulps.

Table 3 shows the starting pH of the storage trials for the different pulps. Low, medium and high are used in the figures below to describe the variation in pH. Before storage, the pH value was adjusted to one of three levels. *Table 3* shows the pH values after adjustment. The adjustment was performed in the same way for all pulps but gave somewhat different pH values for the different pulps.

Fig 1 shows the change in pH during storage of the pulps at 5% pulp consistency. The pH value decreased with time for the bleached pulps indicating an acidification accompanying the heat-induced ageing. This was most evident at a high storage temperature and for the pulp samples with a high pH. It is also noteworthy that storage at low pH does not change the pH of the pulp suspension to any great extent regardless of whether the pulp is bleached or not. It appears as though all pulps tend towards a slightly acidic pH, which is probably towards the equilibrium of carboxylic acid. Many degradation products of polysaccharides contain acidic groups such as the carboxylic group (Fengel, Wegener 1989). The pH of a dithionite-bleached pressurised groundwood pulp, diluted with paper machine white water, was reported to decrease from 6.8 to 6.0 after 11 h storage at 55°C (Pitkänen et al. 1999).

Fig 2 shows the brightness as a function of storage time for the bleached pulp 74.1% ISO stored at a pulp consistency of 5% and at different temperatures – for 65°C, pH was varied too. The time and temperature were the variables with the most pronounced effect on the brightness during pulp storage. A storage time of four hours gives rise to a brightness decrease of 0-2.2% ISO.

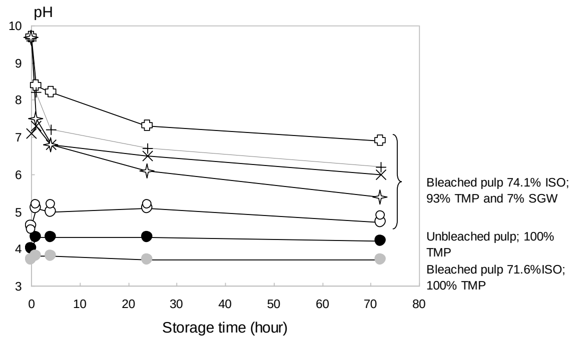

Fig 1. pH as a function of storage time for spruce mechanical pulp, unbleached and hydrogen-peroxide bleached to two brightness levels, stored at 5% consistency at different pH levels (cf. *Table 3*). Some experiments were performed on two different occasions, represented in the figure by large and small symbols. Bleached pulp 74.1% ISO: 50°C high pH (✧); 65°C high pH (+); 65°C medium pH (×); 80°C high pH (✧); 65°C low pH (○ ○). Bleached pulp 71.6% ISO: 65°C low pH (●). Unbleached pulp: 65°C low pH (●).

The influence of pH or of increasing the pulp consistency (results not shown here) were small, with a maximum brightness decrease of about 0.5% ISO for a storage time of four hours. No clear effects could be seen with regards to pH or pulp consistency. In a study by Gellerstedt et al. (1983) the smallest change in relative color formation was found at pH 5.5. In that study hydrogen-peroxide bleached stone groundwood pulp was stored at 0.9% pulp consistency for 4 hours at 80°C and at constant pH achieved by adding acid or base. Also in a study by Narvestad et al. (2011) the smallest decrease in brightness was achieved at pH 5-5.5 (measured after storage). In their study hydrogen-peroxide bleached TMP was stored at 55°C and 65°C for 5 hours at 4% pulp consistency, diluted either with distilled water or with clear filtrate from paper machine. In the studies by Lunan et al. (1986) and Harris and Karnis (1986), a higher pulp consistency resulted in a greater loss of brightness. However, in the study by Lunan et al., the brightness loss was unaffected by pulp consistency in the range 14-50%.

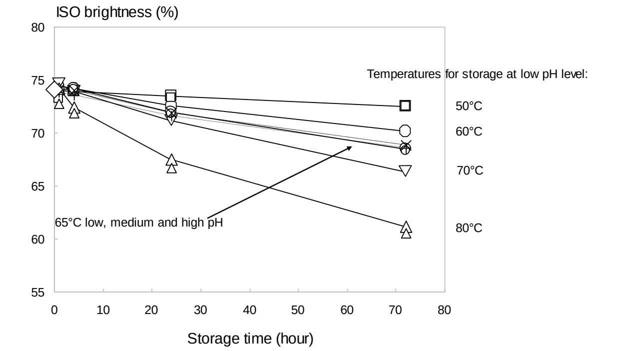

Fig 2. The ISO brightness as a function of storage time for hydrogen-peroxide bleached spruce mechanical pulp (TMP/SGW pulp: 93/7) stored at 5% consistency at different pH levels (cf. *Table 3*). Some of the experiments were performed on two different occasions, represented in the figure by large and small symbols. Bleached pulp 74.1% ISO: 50°C low pH (□ □); 60°C low pH (⬠); 65°C low pH (○ ○); 70°C low pH (▽); 80°C low pH (△ △); 65°C medium pH (╳); 65°C high pH (+). Untreated reference pulp: (◇).

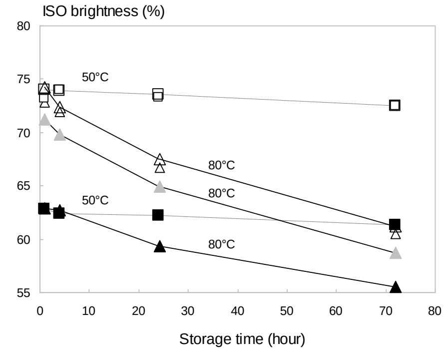

Fig 3. The ISO brightness as a function of storage time for spruce mechanical pulp, unbleached and hydrogen-peroxide bleached to two brightness levels, stored at 5% consistency, 50°C and 80°C at low pH (cf. *Table 3*). Some experiments were performed on two different occasions, represented in the figure by large and small symbols. Bleached pulp 74.1% ISO (TMP/SGW pulp: 93/7): 50°C (□ □); 80°C (△ △). Bleached pulp 71.6% ISO (TMP): 80°C (▲). Unbleached pulp (TMP): 50°C (■); 80°C (▲).

In both these studies, unbleached pulp was taken out at the refiner. In the present study, the influence of pulp consistency in the range 5-25% was evaluated only for the pulp bleached to 74.1%. This pulp is taken out after addition of chelating agent in the mill, and it is also washed in the laboratory and then diluted with distilled water. Maybe the results would have been different if process water was used for dilution. A pulp taken out after refining is not as clean as the bleached and washed pulp used in the present study. When the refiner pulp is diluted with water, a higher pulp consistency means less of the clean water, which could explain the results achieved.

Fig 3 shows the brightness as a function of storage time for the different pulps stored at a pulp consistency of 5%, at low pH and at 50°C and 80°C. The unbleached pulp showed no brightness loss after four hours at either of the storage temperatures. At longer storage times, the temperature 80°C resulted in a measurable brightness loss, whereas storing at 50°C only gave a negligible reduction in brightness. The temperature during storage was important also for the unbleached pulp when storing for longer times. The bleached pulps were more sensitive to storage compared to the unbleached pulp at temperatures above 50°C. At 80°C after 4 h, the brightness decreased with ca. 2% ISO for both bleached pulps. These results are in agreement with ageing of pulp sheets; Forsskåhl et al. (1999) studied the thermal yellowing of unbleached SGW pulp, TMP, chemithermomechanical pulp and hydrogen-peroxide bleached TMP in the temperature interval 60-250°C. The bleached pulp was most sensitive to yellowing but was also affected at lower temperatures than the unbleached pulps in that case.

To distinguish whether changes in the sheet structure or formation of colour causes the observed decreases in brightness, the Kubelka-Munk model (Kubelka, Munk 1931; Kubelka 1948) can be used to describe the light absorption coefficient and the light scattering coefficient.

The light scattering coefficient (s) is related to the structure of the sheet whereas the light absorption coefficient (k) describes the amount of chromophores absorbing light at a given wavelength distribution.

Fig 4 shows the light absorption coefficients at 460 nm plotted against storage time for the different pulps stored at 50°C and 80°C. *Fig 5* is similar, but the light absorption coefficient at 460 nm is plotted against storage temperature. The k-values increased with storage time and temperature in all experiments, indicating formation of coloured groups as expected.

The decrease in brightness could not be attributed to a decrease in s. Storage at 50°C gave only minor increases in k for all pulps, even at the longest times. The high temperature, 80°C, gave higher k-values at all times and also a more rapid increase, especially during the first hours of storage. A comparison of the highly bleached pulp (open symbols) and the unbleached pulp at 80°C shows that the k-value of the bleached pulp increased more for 1 to 24 h. At longer times, the slopes were similar for both pulps. This resembles the behaviour in heat- or light-induced ageing of sheets, where two kinetic phases are seen in the discolouration (Ek 1992). The discolouration process was found to proceed in two phases, with a large brightness drop in the first phase and a slower second phase (Paulsson, Ragauskas 1998). The more rapid initial increase may, at least partly, be due to the higher amount of leucochromophores available in the highly bleached pulp (see e.g. Gellerstedt 1983; Gellerstedt 2009).

The slightly less bleached pulp (71.6% ISO, grey symbols) showed a similar behaviour as the highly bleached pulp (74.1% ISO, open symbols) up to 24 h of ageing, but then continued to increase at the same rate, to finally reach a k-value about 1 unit below the unbleached pulp after 72 h. This higher sensitivity to darkening could be due to the higher Fe-content of this pulp (21 mg/kg, see *Table 2*) as compared to the highly bleached pulp,

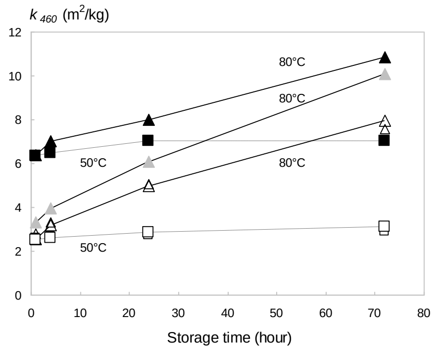

Fig 4. The light absorption coefficient (*k*) at 460 nm as a function of storage time for spruce mechanical pulp unbleached and hydrogen-peroxide bleached to two brightness levels, stored at 5% consistency, 50°C and 80°C at low pH (cf. *Table 3*). Some experiments were performed on two different occasions, represented in the figure by large and small symbols. Bleached pulp 74.1% ISO (TMP/SGW pulp: 93/7): 50°C (□ □); 80°C (△ △). Bleached pulp 71.6% ISO (TMP): 80°C (▲). Unbleached pulp (TMP): 50°C (■); 80°C (▲).

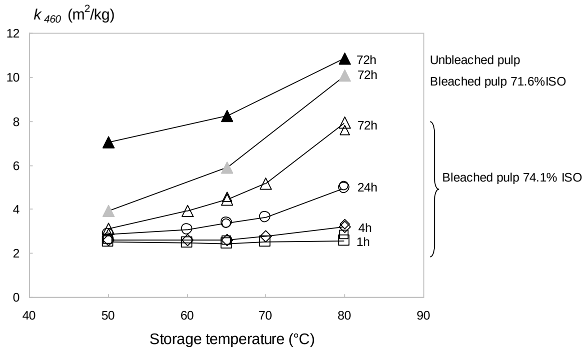

Fig 5. The light absorption coefficient (*k*) at 460 nm as a function of storage temperature for spruce mechanical pulp unbleached and hydrogen-peroxide bleached to two brightness levels, stored at 5% consistency at low pH (cf. *Table 3*). Some experiments were performed on two different occasions, represented in the figure by large and small symbols. Bleached pulp 74.1% ISO: 1 hour (□ □); 4 h (◇◇); 24 h (○ ○); 72 h (△ △). Bleached pulp 71.6% ISO: 72 h (▲). Unbleached pulp: 72 h (▲).

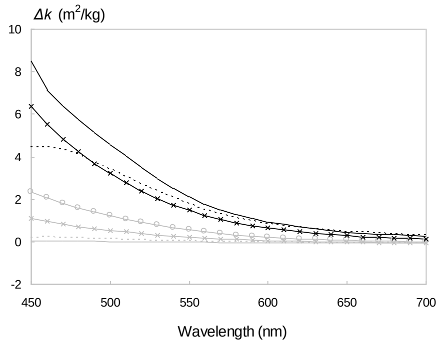

Fig 6. Difference spectra (k_{stored}-$k_{unstored}$) for spruce mechanical pulps, unbleached and hydrogen-peroxide bleached to two brightness levels, stored at 5% consistency and at low pH (cf. *Table 3*). Bleached pulp 74.1% ISO (TMP/SGW pulp: 93/7): 65°C, 1 hour (——); 65°C, 4 h (……); 65°C, 24 h (—×—); 65°C, 72 h (—○—); 80°C, 72 h (—×—). Bleached pulp 71.6% ISO (100% TMP): 80°C, 72 h (——). Unbleached pulp (100% TMP): 80°C, 72 h (……).

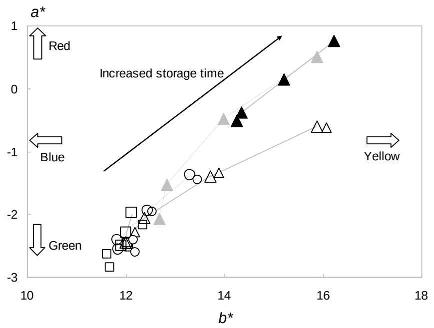

Fig 7. The colour co-ordinates *a** and *b** as a function of storage time for spruce mechanical pulps, unbleached and hydrogen-peroxide bleached to two brightness levels, stored at 5% consistency at low pH (cf. *Table 3*). Some experiments were performed on two different occasions, represented in the figure by large and small symbols. Bleached pulp 74.1% ISO (TMP/SGW pulp: 93/7): 50°C (□ □); 65°C (○ ○); 80°C (△ △). Bleached pulp 71.6% ISO (100% TMP): 80°C (▲). Unbleached pulp (100% TMP): 80°C (▲).

which had the lowest Fe-content in this investigation (11 mg/kg). Iron is well known to cause darkening of mechanical pulps (see e.g. Gupta 1970; Narvestad et al. 2013) and has been shown to be one major reason behind the loss of brightness in this mill system.

Fig 5 shows the effect of temperature in more detail; the increase in *k* was non-linear at all storage times longer than 1 hour. The *k*-values increased with a noticeably steeper slope above a temperature of 65-70°C, and the effect became more pronounced at longer times.

To reduce chromophore formation, the storage temperature should be kept low and the storage time short.The corresponding results for time and temperature in a mill system were presented by Narvesatd et al. (2011). The effects of pH and pulp consistency were investigated for the highly bleached pulp and were small in this clean system.

In *Fig 6*, the formation of chromophores at different wavelengths is shown as the change in the light absorption coefficient, $\Delta k = k_{stored}$-$k_{unstored}$. The values below 450 nm were unreliable as the light absorption was too strong, see e.g. Rundlöf and Bristow (1997), Karlsson *et al.* (2012). Therefore, these values were rejected.

The grey curves represent storage at 65°C for different times, the black curves show data for storage at 80°C for 72 h and are included for comparison. As seen in the figure, there was a general increase in light absorption with storage time in the wavelength region studied (cf. *Fig 4*). The increase in *k* began at short wavelengths. After storage over longer periods of time, the increase in *k* gradually became noticeable also at longer wavelengths. After the longest time at the highest temperature, the *k*-value had increased over the whole wavelength region studied. The increase was smooth, and

Table 4. The lightness values *L** at 1 hour and 72 h (first and last point) for the pulps in *Fig 7*.

Pulp	*L** at 1 h	*L** at 72 h
Unbleached pulp 80°C	91.3	88.4
Bleached pulp 71.6% ISO 80°C	94.5	90.0
Bleached pulp 74.1% ISO 50°C	94.8	94.9
Bleached pulp 74.1% ISO 65°C	95.5	93.6
Bleached pulp 74.1% ISO 80°C	94.9	91.0

no specific peaks could be seen. When the pulps were stored at 80°C for 72 h, the increase in k at shorter wavelengths was higher for the pulp bleached to 71.6% ISO compared to the other two pulps.

The changes in light absorption naturally lead to a change in colour of the pulp. If more light is absorbed at shorter wavelengths, the wavelength distribution of the reflected light will shift towards longer wavelengths, which are not absorbed to the same extent. This is shown in *Fig 7*, where the CIE colour co-ordinates a^* and b^* are plotted for different storage times and temperatures. Initially during ageing of the pulp, the colour was shifted towards red and somewhat towards yellow. At longer times the shift towards yellow became larger (cf. *Fig 6*). The pulp bleached to 71.6% ISO was initially close to the curve of the highly bleached pulp, but approached the curve of the unbleached pulp upon ageing at 80°C, and reached it after 24 h. This behaviour was the same as in the case of k at one wavelength, 460 nanometres (see *Fig 4*). The formation of chromophores naturally also gave a decrease in lightness L^*, see *Table 4*. The change in colour upon ageing was clearly visible under the process conditions studied, also in this clean system.

Conclusions

Elevated temperature and a long storage time influenced the loss of brightness of the well-washed mechanical pulps the most. The decrease in brightness in this clean system was moderate, less than 0.5 units for the brightest pulp (74.1% ISO) under conditions considered "typical" for a mill (50-65°C, 4 h). The result could be used as a benchmark for ideal pulp storage conditions when trying to reduce pulp darkening in mills. At longer times and higher temperatures, the decrease in brightness became larger (13.5 units) at the highest temperature (80°C) and the longest storage time (72 h). At 50°C, the loss of brightness was small or negligible. Pulp consistency and starting pH showed no clear effects in the interval and under the conditions studied.

The darkening was due to an increase in the light absorption coefficient (k). This increase was most rapid initially, during the first four hours, for all pulps when stored at high temperature, and then proceeded more slowly. During the first four hours of storage, the increase in k was most pronounced at short wavelengths but became noticeable also at longer wavelengths for longer storage times. No specific peaks were seen in Δk spectra.

CIE L^*, a^*, b^* data showed that the storage changed the colour of the pulp first towards red and somewhat towards yellow and then more towards yellow. The change in colour was clearly visible.

A slightly less hydrogen-peroxide bleached pulp (71.6% ISO) darkened more than the highly hydrogen-peroxide bleached pulp (74.1% ISO) at all wavelengths and eventually approached the curve for the unbleached pulp. The only difference measured was that this pulp contained more iron than the others, and it is suggested that the iron-content may be at least part of the reason for the more extensive darkening. The system examined in this paper is very clean with a well-washed pulp and controlled laboratory storage conditions. It is therefore important to remember that the effects could be different in a mill system.

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Literature

Beyer, M., Bäurich, C. and Fischer, K. (1995): Mechanism of light and heat induced discoloration of pulp, Das Papier 49(10A), 8.

Chong, J.M., Nanayakkara, N.P.D. and Whiting, P. (1991): Model compound studies of thermal reversion chemistry, J. Pulp Pap. Sci. 17(1), 18.

Ek, M. (1992): Some aspects on the mechanism of photoyellowing of high-yield pulps, Diss., Royal Institute of Technology, Stockholm, Sweden.

Fengel, D. and Wegener, G. (1989): Wood – Chemistry, Ultrastructure, Reactions, Walter de Gruyter, Berlin and New York, pp. 268-295.

Ferritius, R. and Lundström, F. (2011): The effect of hydrogen peroxide containing filtrates and storage on unbleached and bleached pulp brightness, Int. Mech. Pulp. Conf., Xian, China, June 26-29, China Light Industry Press, Xian, China, pp. 255-258.

Fischer, K., Koch, H. and Beyer, M. (1995): Mechanism of light and heat induced yellowing – A comparison, 8th Int. Symp. Wood Pulp. Chem., Helsinki, Finland, June 6-9, Gummerus Kirjapaino Oy, Jyvaskyla, Finland, pp. 429-434.

Forsskåhl, I. (2000): Brightness reversion, In: Stenius, P. (ed.), Forest Products Chemistry, Fapet Oy, Helsinki, Finland, pp. 278-332.

Forsshåhl, I., Korhonen, T. and Tylli, H. (1999): Formation and destruction of chromophores in mechanical pulps by heat and light, 10th Int. Symp. Wood Pulp. Chem., Yokohama, Japan, June 7-10, Japan Technical Association of pulp & Paper Industry, PAPTAC, TAPPI, Yokohama, Japan, pp. 688-693.

Forsskåhl, I., Tylli, H. and Olkkonen, C. (2000): Participation of carbohydrate-derived chromophores in the yellowing of high-yield and TCF pulps, J. Pulp Pap. Sci. 26(7), 245.

Gellerstedt, G. (2009): Mechanical pulping chemistry, In: Ek M., Gellerstedt G. and Henriksson G. (eds.), Pulp and Paper Chemistry and Technology – Volume 2 Pulping Chemistry and Technology, Walter de Gruyter, Berlin, Germany, pp. 35-56.

Gellerstedt, G. and Pettersson, B. (1980): Autoxidation of lignin, Svensk Papperstidning 83(11), 314.

Gellerstedt, G., Pettersson, I. and Sundin, S. (1983): Light-induced and heat-induced yellowing of mechanical pulps, Svensk Papperstidning 86(15), 57.

Gratzl, J.S. (1985): Lichtinduzierte vergilbung von zellstoffen – Ursachen und verhütung, Das Papier 39(10A), 14.

Grossmann, K. and Ott, G. (1994): A comparison of light and heat induced yellowing of different pulps, Das Papier 48(10), 623.

Gupta, V.N. (1970): Effect of metal ions on brightness, bleachability and colour reversion of groundwood, Pulp Pap. Mag. Can. 71(18), 69.

Harris, G. and Karnis A. (1986): Storage of latent mechanical pulps, J. Pulp Paper. Sci. 12(4), 100.

Hill, J., Sabourin, M., Johansson, L., Mörseburg, K., Axelsson, P., Aichinger, J., Braeuer, P. and Gorski, D. (2010): Combining selective bleaching chemistries and ATMP technology for low energy mechanical pulping at higher brightness, 7th Int. Sem. Fund. Mech. Pulp Res., Nanjing, China, June 20-26, Chinese Academy of Forestry, Nanjing, China, pp. 170-182.

Holmbom, B., Ekman, R. and Eckerman, C. (1992): Degradation products formed during lignin and heat treatments of spruce groundwood, J. Pulp Pap. Sci. 18(4), 146.

Hon, D.N.S. (1979): Discoloration and bleaching of thermomechanical pulps, Southern Pulp Paper Mfr. 42(3), 23.

Hon, D.N.S. (1991): Color and discoloration, In: Hon D.N.S. and Shiraishi, N. (eds.), Wood and Cellulosic Chemistry, Marcel Dekker Inc., New York, USA, pp. 395-454.

Hon, D.N.S. and Glasser, W. (1979): On possible chromophoric structures in wood and pulps – A survey of the present state of knowledge, Polym. Plast. Technol. Eng. 12(2), 159.

Johnsen, I.A., Narvestad, H., Axelsson, P., Enberg, S., Aasarød, K. and Kure, K-A. (2010): Metal induced brightness loss of peroxide bleached TMP, 7th Int. Sem. Fund. Mech. Pulp Res., Nanjing, China, June 20-26, Chinese Academy of Forestry, Nanjing, China, pp. 211-218.

Karlsson, A., Enberg, S., Rundlöf, M., Paulsson, M. and Edström, P. (2012): Determining optical properties of mechanical pulps, Nord. Pulp Paper Res. J. 27(3), 531.

Kubelka, P. and Munk, F. (1931): Ein beitrag zur optik der farbanstriche, Z. Tech. Phys. 12(11a), 593.

Kubelka, P. (1948): New contributions to the optics of intensely light-scattering materials – Part 1, J. Opt. Soc. Am. 38(5), 448.

Kuizhong, S., Guigan, F. and Ping, L. (2010): Bleaching of CTMP pulps from nine wood species. 7th Int. Sem. Fund. Mech. Pulp Res., Nanjing, China, June 20-26, Chinese Academy of Forestry, Nanjing, China, pp. 196-201.

Lee, J., Balatinecz, J.J. and Whiting, P. (1989): The optical properties of eight Canadian wood species – IV – Brightness stability. 5th Int. Symp. Pulp. Chem., Raleigh, USA, May 22-25, pp. 529-533.

Lunan, W.E., Sferrazza, M.J., Fransén, R.G. and May, W.D. (1986): Curl-setting during storage of thermomechanical pulp at high consistency, J. Pulp Pap. Sci. 12(4), 108.

Luo, C., Putz, L. and Göttsching, L. (1988): Investigations of the light and heat-induced yellowing of bleached high-yield pulps, Das Papier 42(10A), 55.

Moldenius, S. (1983): Light absorption coefficient spectra of hydrogen peroxide bleached mechanical pulps, Paperi Puu 65(11), 747.

Narvestad, H., Axelsson, P. and Kure, K-A. (2011): Full scale experiences with magnesium hydroxide based peroxide bleaching and TMP brightness loss at Norske Skog Saugbrugs, Int. Mech. Pulp Conf., Xian, China, June 26-29, China Light Industry Press, Xian, China, pp. 287-290.

Narvestad, H., Gregersen, Ø.W. and Kure, K-A. (2013): Filler clay induced discolouration of bleached mechanical pulp, Nord. Pulp Paper Res. J. 28(1), 68.

Paulsson, M. and Parkås, J. (2012): Review: Light induced yellowing of lignocellulosic pulps – Mechanisms and preventive methods, BioRes. 7(4), 5995.

Paulsson, M. and Ragauskas, A.J. (1998): Chemical modification of lignin rich-paper – Part 9 – Effect of dry heat and moist heat on the accelerated yellowing of untreated and acetylated high-yield pulps, Nord. Pulp Pap. Res J. 13(3), 191.

Pitkänen, M., Mannström, M. and Lumiainen J. (1999): Thickening, storage and post refining, In: Sundholm J., (ed.), Mechanical pulping, Fapet Oy, Helsinki, Finland, pp. 345-362 and references therein.

Polcin, J. and Rapson, W.H. (1971): Sapwood and heartwood groundwood of western hemlock and jack pine – part II – Heat stability of extractives, Pulp Paper Mag. Can. 72(10), 84.

Rundlöf, M. and Bristow, J.A. (1997): A note concerning the interaction between light scattering and light absorption in the application of the Kubelka-Munk equations, J. Pulp Paper Sci. 23(5), 220.

Tylli, H., Forsskåhl, I. and Olkkonen, C. (1997): Effect of heat, light and infrared radiation on chemimechanical pulp studied by fluorescence spectroscopy, 9th Int. Symp. Wood Pulp. Chem., Montréal, Canada, June 9-12, Technical Section, CPPA, Montreal, Canada, pp. 116-1-116-4.

Yoon, B.H., Wang, L.J. and Kim, G.S. (1999): Formation of lignin-metal complexes by photo-irradiation and their effect on colour reversion of TMP, J. Pulp Pap. Sci. 25(8), 289.

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