The influence of process waters on optical properties during storage of hydrogen-peroxide bleached Norway spruce mechanical pulp

Sofia Enberg, Mats Rundlöf, Magnus Paulsson, Patrik Axelsson, Øyvind Eriksen and Per Engstrand

SUMMARY: To evaluate the causes behind the formation of colour in mill systems, the effect of different process waters on the optical properties of hydrogen-peroxide bleached Norway spruce mechanical pulp during storage was studied. The influence of process water type, temperature, time, pulp consistency and pH was evaluated over the visible range of wavelengths. The darkening was more pronounced when pulp was stored in process waters compared to in distilled water. Increased temperature and prolonged storage times increased the darkening as expected, whereas a higher storage consistency gave less darkening than a lower storage consistency (15% compared to 5%). The pH value that gave the lowest brightness reduction and a minimum in Δk_{460} was found to be 5.5–6.0. Storage of pulp in white water from the paper machine resulted in a broad shoulder in the k spectra indicating colour formation related to the particles in this water. Part of this shoulder in absorption spectra was related to added dyes, but the increase in absorption with time is likely to be caused by some other colour formation. The colour measured as $a*$, $b*$ showed that the storage changed the colour of the pulp towards red and yellow, and initially more towards red.

ADRESSES OF THE AUTHORS:
Sofia Enberg (sofia.enberg@norskeskog.com): Norske Skog Saugbrugs, NO-1756 Halden, Norway / FSCN, Mid Sweden University, SE-851 70 Sundsvall, Sweden
Mats Rundlöf (mats@capisco.se): Capisco Science & Art, SE-602 34 Norrköping, Sweden / FSCN, Mid Sweden University, SE-851 70 Sundsvall, Sweden
Magnus Paulsson (magnus.paulsson@akzonobel.com): AkzoNobel Pulp and Performance Chemicals, SE-445 80 Bohus, Sweden / FSCN, Mid Sweden University, SE-851 70 Sundsvall, Sweden
Patrik Axelsson (patrik.axelsson@norskeskog.com): Norske Skog Saugbrugs, NO-1756 Halden, Norway
Øyvind Eriksen (oyvind.eriksen@pfi.no): Paper and Fibre Research Institute, NO-7491 Trondheim, Norway
Per Engstrand (Per.Engstrand@miun.se): FSCN, Mid Sweden University, SE-851 70 Sundsvall, Sweden
Corresponding author: Sofia Enberg

The market for paper produced from mechanical pulp is declining steeply, especially for newsprint grades (Kallioranta, Ostle 2013) and, at the same time, the brightness (whiteness) demands for mechanical pulp based printing paper have risen (Hill et al. 2010; Johnsen et al. 2010; Kuizhong et al. 2010). It is therefore important to be able to produce mechanical pulp with high brightness in a cost-efficient and environmentally-friendly way. One drawback of mechanical pulp and mechanical pulp based paper is discolouration due to ultraviolet radiation and heat (see e.g. Forsskåhl 2000; Paulsson, Parkås 2012). Mill experience shows that the brightness of bleached mechanical pulp is often reduced along the process line from the bleach tower to the paper machine (Johnsen et al. 2010; Narvestad et al. 2011). This is a well-known and costly phenomenon (Narvestad et al. 2013a) and there may be several reasons for the discolouration, which most probably varies within one mill from time to time and from one mill to the next.

The brightness of unbleached and dithionite and/or hydrogen peroxide bleached softwood mechanical pulps has been reported to decrease during pulp storage (Gellerstedt et al. 1983; Harris, Karnis 1986; Lunan et al. 1986; Johnsen et al. 2010; Narvestad et al. 2011; Enberg et al. 2013; Narvestad et al. 2013a; Narvestad et al. 2013b; Narvestad et al. 2013c). In a previous study (Enberg et al. 2013) the effect of process conditions on the storage of chelated and well-washed, unbleached and hydrogen-peroxide bleached Norway spruce mechanical pulps was studied. Time and temperature (50–80°C) were the process variables that had the largest impact on the discolouration whereas pH (4.3–9.7 at the beginning of storage) and pulp consistency (5–25%) were of minor importance. The pulps bleached with hydrogen-peroxide were more sensitive to storage compared to the unbleached pulp at temperatures above 50°C (cf. Gellerstedt, Pettersson 1980). Harris and Karnis (1986) found that when latent unbleached thermomechanical pulp (TMP) was stored at 80°C and at high consistency (40%), a loss in pulp strength due to residual fibre curl and a decrease in brightness due to an increase in the light absorption coefficient occur. The authors also reported that the light scattering coefficient was unchanged and that there was good correlation between the results obtained in mill trials and those obtained in controlled laboratory trials. Similar results were reported by Lunan et al. (1986) when storing unbleached TMP at high consistency (50%) at temperatures exceeding 65°C, i.e. that the aged pulp developed a residual latency due to curl-setting and that this was not removable by longer periods of disintegration. Further, a strong correlation between the storage temperature and the brightness loss was observed; storage at 50°C did not lower the brightness, while temperatures exceeding 80°C strongly discoloured the pulp. The changes in the light scattering coefficient were minor for all aging temperatures in the interval 50–100°C (Lunan et al. 1986). Storing hydrogen-peroxide bleached TMP at low consistency (~4%) was reported to result in brightness losses already at 55°C (Johnsen et al. 2010; Narvestad et al. 2011) and

increasing the temperature to 65°C aggravated the discolouration (Narvestad et al. 2011). The extent of reversion was due to pH and the type of dilution water; the brightness stability was highest when pH was 5.0–5.5 (cf. Gellerstedt et al. 1983) and when the pulp was diluted with clear filtrate instead of unfiltered process water. Furthermore, there was good correlation between the results obtained in laboratory trials and the results obtained at the mill (Johnsen et al. 2010; Narvestad et al. 2011).

In addition to discolouration caused by elevated temperatures, components in the dilution water may affect the discolouration either directly, upon contact with the pulp, or by accelerating the heat-induced reactions. Transition metal ions are known to accelerate the heat and alkali-induced darkening (Gupta 1970; Ni et al. 1997) of mechanical pulp, and iron in both ferrous and ferric form affect the colour and discolouration when storing high yield pulps (Gupta 1970; Gellerstedt, Pettersson 1980; Gellerstedt et al. 1983; Johnsen et al. 2010; Narvestad et al. 2013a; Narvestad et al. 2013b). Metal ions in a concentration typical for tap water (Fe: ~0.3 mg/l; Cu: ~0.04 mg/l) are sufficient to reduce the pulp brightness by up to four units and accelerate the heat-induced yellowing of various types of high-yield pulps (Ni et al. 1997). Hydrogen-peroxide bleached pulps were found to be more sensitive compared to unbleached pulps, probably due to the formation of new functional groups (e.g. phenolic hydroxyl groups) during bleaching that could participate in auto-oxidation reactions or form coloured metal ion complexes. Others have reported that reductively (dithionite) bleached pulps are more sensitive to metal ions in process waters compared to oxidatively bleached (hydrogen peroxide) pulps, and this was ascribed to a more extensive formation of coloured metallic complexes with lignin structures in the dithionite-bleached pulps (Mao, Ni 2008). Furthermore, Johnsen et al. (2010) reported a brightness reduction when mechanical pulp was stored together with a non-specified paper additive containing significant amounts of metals. Narvestad et al. (2013a) reported that filler clay may induce discolouration by up to seven units of brightness in a Norway spruce mechanical pulp. The clay-induced brightness reduction was attributed to the dissolution of iron from the clay. Furthermore, other metals (e.g. copper) and organic components (e.g. dissolved lignin and extractives) in process waters as well as residual bleaching and paper chemicals may influence heat-induced discolouration during pulp storage (Johnsen et al. 2010; Gellerstedt, Pettersson 1980; Ni et al. 1997; Rundlöf et al. 2000a; Rundlöf et al. 2000b). The darkening of precipitated calcium carbonate and precipitated calcium sulfate in the wet end of a paper machine was attributed to the adsorption of wood based dissolved and colloidal substances from the water phase onto the surface of the fillers (Varhimo et al. 2012). Residual hydrogen peroxide in process water may, however, improve the brightness of unbleached pulp during storage (Ferritius, Lundström 2011).

There are different opinions regarding the mechanisms for heat-induced discolouration of high-yield pulp. One is

that the mechanism for heat-induced darkening is caused by the formation of chromophores in lignin (Gellerstedt, Pettersson 1980; Gellerstedt et al. 1983; Gratzl 1985; Chong et al. 1991). Another opinion is that the mechanism also involves carbohydrates (Luo et al. 1988; Holmbom et al. 1992; Grossmann, Ott 1994; Beyer et al. 1995; Forsskåhl et al. 2000). Gellerstedt and Pettersson (1980) showed that hydroquinone and catechol structures in lignin may give rise to rapid discolouration of lignin-rich pulps when exposed to oxygen due to the formation of *para-* and *ortho*-quinones as the primary reaction products and that the auto-oxidation was accelerated in the presence of heavy metal ions. It has been shown that phenoxyl radicals are formed during heat-induced aging of mechanical pulp and that these radicals are transformed into quinones (Gellerstedt et al. 1983). Transition metal ions, especially ferrous and ferric ions, form strongly coloured complexes with lignin and extractives (Gore, Newman 1964; Gupta 1970; Polcin, Rapson 1972; Meshitsuka, Nakano 1973; Hon, Glasser 1979; Moldenius 1983; Zhang, Gellerstedt 1994; Gosh, Ni 1998; Ni el al. 1999; Yoon et al. 1999; Forsskåhl 2000; Peart, Ni 2001; Friman et al. 2004) and may therefore contribute to the colour and discolouration of mechanical pulp as well as lignin and extractive model compounds. In general, the absorption bands of these complexes are broad, often covering the whole visible spectrum (Polcin, Rapson 1972; Moldenius 1983; Ghosh, Ni 1998; Ni et al. 1999; Peart, Ni 2001; Friman et al. 2004).

The purpose of this work is to evaluate the effect of different process waters on the optical properties of a hydrogen-peroxide bleached Norway spruce mechanical pulp during storage; this was done to obtain a more detailed description of the causes behind the formation of colour in mill systems. The influence of process water type, temperature, time, pulp consistency and pH was evaluated over the visible range of wavelengths.

Material and Methods

Materials

Pulp

Mechanical pulp made from Norway spruce (*Picea abies*) was taken from a mill producing super calendered (SC) paper. The hydrogen-peroxide bleached pulp was collected from the wash press after a high consistency bleach tower. The pulp consisted of 93% thermomechanical pulp and 7% groundwood pulp. Magnesium hydroxide was used as the alkali source during hydrogen-peroxide bleaching. The pulp was washed in two stages before further treatment in order to reduce the metal content and amount of dissolved organic material. The first washing stage (Q) was performed with 2.0 kg/bdt diethylenetriaminepentaacetic acid, penta-sodium salt (Dissolvine D-40-K from AkzoNobel Functional Chemicals, Amersfoort, the Netherlands) at 4% pulp consistency (p.c.) at 50°C for 30 min. The second stage (W) was performed with distilled water at 3% p.c. at 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 recirculated 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. For comparison, some experiments were also performed on the unwashed pulp. Distilled water was used in all pulp washing and laboratory trials described below unless otherwise stated.

Process waters

Process waters were taken from different positions in the production line at a mill producing SC paper. The process waters were chosen to represent a variety in composition and character. The process waters were: white water from the paper machine (WW PM), clear filtrate from the paper machine (CF PM), bleach filtrate from the wash press after hydrogen-peroxide bleaching (Bleached filtrate) and clear filtrate from TMP (CF TMP). The residual hydrogen peroxide in Bleached filtrate and CF TMP was decomposed by addition of the enzyme catalase. Any possible effects from having residual hydrogen peroxide present during storage were therefore not studied here. The process waters were used in the storage trials both as received and after centrifugation (1500 G (3040 rpm) for 10 min) to obtain the dissolved and colloidal phase with a very low content of solid particles such as fines or fillers. Some of the waters were collected on two different occasions (named A and B).

Methods

Metal, sulfur and nitrogen analyses

The metal and sulfur contents of pulp and process waters were analysed after wet combustion with nitric acid (65% concentration, trace analysis, from Fluka Analytical) using a microwave system with an inductively coupled plasma (ICP) instrument (IRIS Advantage s/n 10973). The report limits in pulp (mg/kg) for Ca, Cu, Fe, K, Mg, Mn and Na were 20, 0.1, 0.5, 10, 20, 0.1 and 5 respectively. The report limits in process water (mg/l) for Al, Ca, Cu, Fe, Mg, Mn, Na, S and Si were 0.04, 0.2, 0.02, 0.04, 0.1, 0.02, 2, 1.3 and 0.2 respectively. The nitrogen content in process waters was analysed according to the standard method SS 28101, Nitrogen content of water – Determination with Kjeldahl method after reduction with Devarda's alloy. The report limit was 7 mg/l.

Standard analyses of process waters

The process waters were analysed according to the following standard methods: Chemical oxygen demand (COD), ISO 15705:2002; suspended solids (SS), ISO 11923:1997/NS 4733:1983; conductivity, ISO 7888:1985 and turbidity, ISO 7027:1999. The ash content was determined by combustion of the SS filter in an oxygen atmosphere.

Chemical analyses of process waters

Gravimetrical determination of the content of extractives was carried out by extracting the samples three times with methyl *tert*-butyl ether (MTBE, from Romil Ltd.) with a pH of 3.5. The combined extracts were then evaporated, dried at 105°C and weighed. The sample volume was 50 ml and 3x40 ml MTBE was used.

The composition of extractives (lignans and lipophilic extractives such as fatty acids, resin acids, sterols, steryl esters and triglycerides) was determined according to the method described by Örså and Holmbom (1994) with the following exceptions: the process waters were analysed as received, i.e. no filtration or centrifugation was applied, but the sample bottles were carefully shaken before samples were taken out. The combined extracts were evaporated using nitrogen steam and the sample was dried with Na_2SO_4 (from Acros Organics) before silylation. 100 μl bis-(trimethylsilyl)-trifluoro-acetamide (from Fluka Analytica) and 50 μl trimethylchlorosilane (from Aldrich Chemistry) was added to the residue and the solution was heated at 70°C for 30 min. After silylation, the sample was cooled down before being transferred to a gas chromatography (GC) injection glass. The GC instrument used was an Agilent Technologies 7890 equipped with a flame ionisation detector and an Agilent Technologies DB-1 column (length 7.5; inner diameter, 0.53 mm; film thickness, 0.15 μm). The temperature profile used was 90°C for 1.5 min, then a temperature increase of 12°C/min to 340°C which was maintained for 5 minutes. The detector temperature was 340°C. The system uses helium as a carrier gas.

The water sample after MTBE extraction was analysed for the amount of lignin-like substances by ultraviolet (UV) spectroscopy at 280 nm (extinction coefficient, 19 l/mg, cm). Before analysis, the pH of the sample was adjusted back to the starting value of the process water with sodium hydroxide (from Merck, pro analysi). The UV absorbance was measured with a UV-1800 Shimadzu instrument.

pH adjustment

In some of the trials, pH was varied to evaluate the effect of pH during storage. The dose of hydrochloric acid or sodium hydroxide (both from Merck, pro analysi) giving pH ~4–8 after storage was optimised for each type of process water. The washed pulp was mixed with process water or distilled water and stored for five minutes at room temperature prior to pH adjustment. Hydrochloric acid or sodium hydroxide was then added to the pulp suspension. The pH after five minutes was recorded as the "starting pH".

Storage trials

The pulp storage trials were performed at controlled temperatures in a water bath. For trials without pH adjustment, the pulp was mixed with water and stored for five minutes at room temperature before pH was measured. After measuring the starting pH, the pulp suspension was transferred to 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 measuring pH and proceeding to sheet formation. For the storage time 0 hours, sheet formation started directly after measuring pH.

Table 1 - Some characteristics of the process waters used. Values in parentheses represent values for the waters after centrifugation. Some waters were taken out on two different occasions named A and B.

	Suspended solids (mg/l)	Ash content (mg/l)	Turbidity (NTU)	COD (mg/l)	pH	Conductivity (mS/cm)
CF TMP	260 (170)	0 (0)	390 (370)	2200 (n.a.1)	5.3 (n.a.1)	0.8 (n.a.1)
Bleached filtrate	600 (110)	32 (13)	400 (280)	3100 (2920)	7.5 (7.6)	2.2 (0.8)
CF PM A	62 (35)	0 (0)	60 (56)	280 (293)	6.2 (n.a.1)	0.6 (n.a.1)
CF PM B	13	6	19	560	5.5	1.1
WW PM A	9600 (12)	7700 (0)	11000 (34)	240 (230)	6.1 (n.a.1)	0.5 (n.a.1)
WW PM B	8900	6100	n.a.1	640	5.4	1.1

[1]not analysed

Distilled water and the four process waters, both as received and after centrifugation, were stored together with the washed pulp for five hours at 5% pulp consistency at 50°C or 65°C. The pulp was also stored at a higher concentration, 15%, at 65°C for 5 h. To each consistency a constant volume of water was added to a certain amount of pulp, and any possible solid material in the waters was not taken into account. Furthermore, the mechanical pulp was stored for longer periods of time in Bleached filtrate, CF PM, WW PM and distilled water at 65°C and 5% pulp consistency: 5, 12 (not for Bleached filtrate), 24, 48, and 72 hours. Storage trials were performed in CF PM, WW PM and distilled water at varying pH-levels, ~4–8 (measured after storage), at 65°C and 5% pulp consistency for 5 hours. In every experiment, sheets were made of the pulp and water mixture before storage (0 hours) and used as a reference. The WW PM and CF PM named A were used in the first trials, corresponding waters named B were used in the trials with longer storage times and in the trials where the pH was varied.

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 187:1990) were produced on a small sheet former according to the method described by Karlsson et al. (2012). The sheet former had a 200 mesh wire with a diameter of 112 mm. To increase the retention of material, a retention chemical was added during disintegration. The retention chemical was a polyamine received from AkzoNobel Pulp and Performance Chemicals (Eka ATC 4150), and the charge was 1.5 kg/bdt. 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% p.c., the retention chemical was added, and the suspension was then disintegrated for one additional minute. A sodium acetate buffer (prepared with 136.08 g CH$_3$COONa x 3H$_2$O, 31.8 ml concentrated CH$_3$COOH 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 with 50% relative humidity as described in standards ISO 5269-1:1998 and ISO 187:1990 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 sec. A 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 two minutes at 410 kPa and dried and conditioned at 23°C with 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 standard procedures ISO 2470:1999, ISO 5631:2000 and ISO 9416:1998 respectively.

Results and Discussion

Characteristics of process waters
The hydrogen-peroxide bleached Norway spruce mechanical pulp was stored together with various types of process waters taken from four positions along the process line:
- Clear filtrate from the TMP mill before bleaching, "CF TMP".
- Filtrate from the press after the bleach tower, "Bleached filtrate".
- Clear filtrate from the paper machine, "CF PM".
- White water from the paper machine, same as above but not filtered, "WW PM".

Table 1 shows some characteristics of the analysed process waters.

Two samples from the pulp mill, CF TMP and Bleached filtrate, contained some suspended solids which could partly be removed by centrifugation. The CF TMP contained only organic solids and the major part of the solids in the Bleached filtrate were organic, but a small ash content could be measured. This inorganic material may at least partly originate from the suspended

Table 2 - The content of some metals, sulfur and nitrogen in the process waters examined. Values in parentheses represent values for the water after centrifugation. Some waters were taken out on two different occasions named A and B.

Me (mg/l)	Al	Si	Fe	Mg	Ca	Na	Mn	Cu	S	N
CF TMP	1.2	5.3	0.74	81	42	n.a.[1]	11	0.08	67	19
Bleached filtrate	0.67	6.1	1.0	230	31	160	2.4	0.04	110	17
CF PM A	4.8	7.2	0.44	33	5.8	n.a.[1]	0.06	0.03	n.a.[1]	n.a.[1]
CF PM B	0.27	4.8	0.39	57	9.3	130	0.28	<0.02	160	<7
WW PM A	0.29	1.6	0.16	28	5.1	55	0.05	0.02	66	n.a.[1]
	(0.74)	(1.0)	(0.24)	(22)	(4.4)	(n.a.)[1]	(0.05)	(0.02)	(53)	
WW PM B	0.46	5.3	1.9	53	8.9	120	0.28	<0.02	140	<7

[1]not analysed

$Mg(OH)_2$ used as an alkali source in the bleach plant, also indicated by the high Mg content in the water phase (see *Table 2*) and possibly the higher pH. The COD values were the highest by far, indicating that the major part of the contents of these two samples were organic. The COD values remained about the same before and after centrifugation, which was the case for all samples, indicating that the COD was caused by dissolved and/or colloidal substances. The COD values of the clear filtrate, CF PM, were on the same level as those of the unfiltered white water, WW PM.

The unfiltered white water from the paper machine, WW PM, contained the highest amounts of suspended solids, and also had the highest turbidity. These suspended solids were inorganic, most probably filler clay, and could be removed almost completely by centrifugation (represented by values in parentheses in *Table 1*). The corresponding clear filtrate, CF PM, contained the smallest amounts of suspended solids, with an ash content close to zero.

Both WW PM and CF PM were taken out on two different occasions (18 months difference), on the first occasion the production was a standard quality of paper whereas on the second occasion it was a high-bright quality produced with an increased charge of bleaching chemicals. There were some differences: the COD and conductivity were lower for both waters at the first sampling; pH and turbidity were higher.

In *Table 2*, the contents of some metals, sulfur and nitrogen for the different process waters are shown. These measurements were made on the clear water phase of the samples, which means that the contribution from any solids was small. In general, the metal content was judged to be within the normal range for this type of process. The higher concentrations of magnesium in the samples from the pulp mill were most probably due to the

$Mg(OH)_2$ used as an alkali source in the bleaching. The content of metals known to cause darkening (Gupta 1970; Ni et al. 1997), iron and copper, was low in all waters. The iron content of WW PM was 0.16 mg/l in the first sample "A" and more than ten times higher, 1.9 mg/l, in the second sample "B". This is still, however, considered to be a low iron content. When as much as possible of the solid material in the WW PM was dissolved in acid, the iron content was much higher: 19 mg/l for WW PM A and 20 mg/l for WW PM B. This shows that the suspended solids contain metals which may affect the pulp if they can be dissolved into the water phase. Nitrogen was measured to indicate if DTPA (diethylene-triaminepentaacetic acid) was present in the sample. The addition of DTPA in the TMP plant is placed before the sample point of both CF TMP and Bleached filtrate. The content of nitrogen was higher for the TMP waters compared to the PM waters, which may indicate that some DTPA is present in these waters. The sulfur content mainly originates from the addition of bisulfite as acidification after hydrogen peroxide bleaching and possibly also from post-bleaching with sodium dithionite on the paper machine. The higher sulfur content in the WW PM B waters can be explained by the higher dose of chemicals used when the high-bright quality was produced.

Table 3 shows contents of extractives and lignin. The content of extractives was much higher in the waters from the TMP plant, Bleached filtrate and CF TMP compared with CF PM and WW PM waters from the paper mill. This corresponds with the high COD and turbidity values (*Table 1*), which was expected as lipophilic extractives are present in the form of colloidal particles also after hydrogen-peroxide bleaching (Thornton et al. 1991). The composition of extractives was considered to be within the normal range for this

Table 3 - The content of lignin and extractives in the process waters.

Process water	Lignin (mg/l)	Gravimetric extractives (mg/l)	Extractives from GC analyse						SUM (mg/l)	% found from gravimetric
			Part of sum (%)							
			Lignans	Steryl esters	Sterols	Tri-glyce-rides	Fatty acids	Resin acids		
CF TMP	328	478	69.6	7.6	6.8	7.2	4.5	4.3	246	51
Bleached filtrate	258	320	49.4	13.0	6.8	14.8	4.5	11.6	126	39
CF PM B	80	63	70.0	5.7	9.5	0.4	7.4	7.4	28.3	45
WW PM B	68	90	33.5	14	6.6	28.2	9.8	7.9	52.8	58

process and wood species (Ekman et al. 1990). The lignin content was also much higher in the TMP waters. In the GC analyses of extractives, only up to ~60% of the extractives found in the gravimetric determination could be detected. Thus, there are some extractives that are not included in the GC determination, for example phenolic compounds such as stilbenes and tannins that may contribute to colour as such or in combination with metals (Polcin et al. 1969; Ni el al. 1999; Friman et al. 2004).

The influence of process waters on pulp brightness and light absorption coefficients

The pulp used in all experiments with only a few exceptions was washed in a two stage procedure. After the two-stage laboratory washing procedure, the concentration of all measured metals was very low, and the wash did not affect the optical properties of the pulp. The iron content was 17 mg/kg before the wash and 11 mg/kg after the wash. The manganese content was 2.8 mg/kg before the wash and 0.2 mg/kg after the wash. The copper content was <0.1 mg/kg both before and after wash. The brightness was 73.9% ISO before the wash and 74.1% ISO after the wash. Detailed characteristics before and after the washing procedure can be found in Enberg et al. (2013).

Fig 1 deals with the changes in brightness and k_{460} evaluated in two different ways: i) the difference between dilution with distilled water and process waters before storage (Fig 1a and b); ii) the effect of storage in different waters over time, i.e. a comparison of optical properties directly after dilution with those after 5 h of storage (Fig 1c and d). When the clear filtrate from the pulp mill, CF TMP, was mixed with the washed pulp, the brightness and k-values were unaffected; the brightness was 75.0% ISO for CF TMP compared to 74.8% ISO for the clean system. For the Bleached filtrate, the brightness decreased to 74.1% ISO and the k_{460}-value increased, this means that the darkening of the pulp was caused by the formation of coloured groups. After centrifugation, the increase in k became higher and the s-value increased (Fig 1b), which caused a smaller brightness loss compared to using the water as received. The Bleached filtrate contained some suspended solids, of which only a small part was inorganic. The increase in s is probably related to the removal of these particles. It is possible that small particles may fill pores in the sheet that would otherwise scatter light. The increase in s of the centrifuged bleached filtrate is also accompanied by a decrease in the sheet density as compared to the water as received. Therefore it may be speculated that the suspended solids could have contributed to the strength of the sheet and thereby a lower s compared with the centrifuged water.

Using CF PM for dilution, the brightness increased to 75.4% ISO whereas the k_{460} remained more or less unchanged. The increase in brightness was attributed to a higher light scattering. The higher light scattering of the CF PM was not caused by filler material present in this water since the ash content was zero (cf. Table 1). It may be related to a lower density and strength, giving a more porous sheet structure. For WW PM, both the brightness (76.1% ISO) and the k_{460} increased. The increase in brightness was most probably due to the light scattering of the filler material present in the WW PM. The s-values at 460 nm, before and after centrifugation, are included in Fig 1b. For the pulp in distilled water, the light scattering coefficient at 460 nm was 71.5 m²/kg, and when WW PM was added the s-value became 92.7 m²/kg. The removal of solid particles by centrifugation naturally gave a lower contribution to the s-value and therefore a lower brightness. Nevertheless, the centrifuged WW PM increased the s-value as compared to the case with distilled water in a similar way to the CF PM (as may be expected).

The light scattering coefficient for pulps stored at 15% pulp consistency are not included in Fig 1b as the value is influenced by the amount of material added, and a higher consistency means less material. For WW PM, the light scattering coefficient at 15% pulp consistency was 79.8 m²/kg as compared to 92.7 m²/kg at 5%. There were some experimental variations in the light scattering coefficients, though the light scattering coefficients did not change in a systematic way as a consequence of storage.

These results shows the importance of using s- and k-values to interpret changes in the measured reflectance factors such as brightness, as the light scattering coefficient varies along the process line. If the fibres darken due to formation of colour and s increases at the same time, the net effect on brightness may be zero or positive, and the formation of colour may therefore pass unnoticed.

The discolouration, measured as an increase in k_{460}, was more pronounced when the pulp was stored in process waters compared to when it was stored in distilled water for all storing conditions studied (Fig 1d). At 50°C, the discolouration was small or negligible. An increase in temperature to 65°C increased the discolouration, as expected. When the pulp was stored at a higher consistency, 15% compared to 5%, the increase in k_{460} was less for all waters, probably because a higher pulp consistency means less dilution with process water and the amounts of material causing discolouration decreases. In a previous study (Enberg et al. 2013), when pulp was stored in a clean system, the pulp consistency in the interval 5–25% was of minor importance. However when process waters are used for dilution, a higher consistency during storage seems to be preferable to preserve a high brightness. This result seems to contradict the results of Harris and Karnis (1986) and Lunan et al. (1986). In both these studies, unbleached 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 (however, in the study by Lunan et al. (1986) the brightness loss was unaffected by pulp consistency in the range 14–50%). 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 water, which could explain the different results achieved.
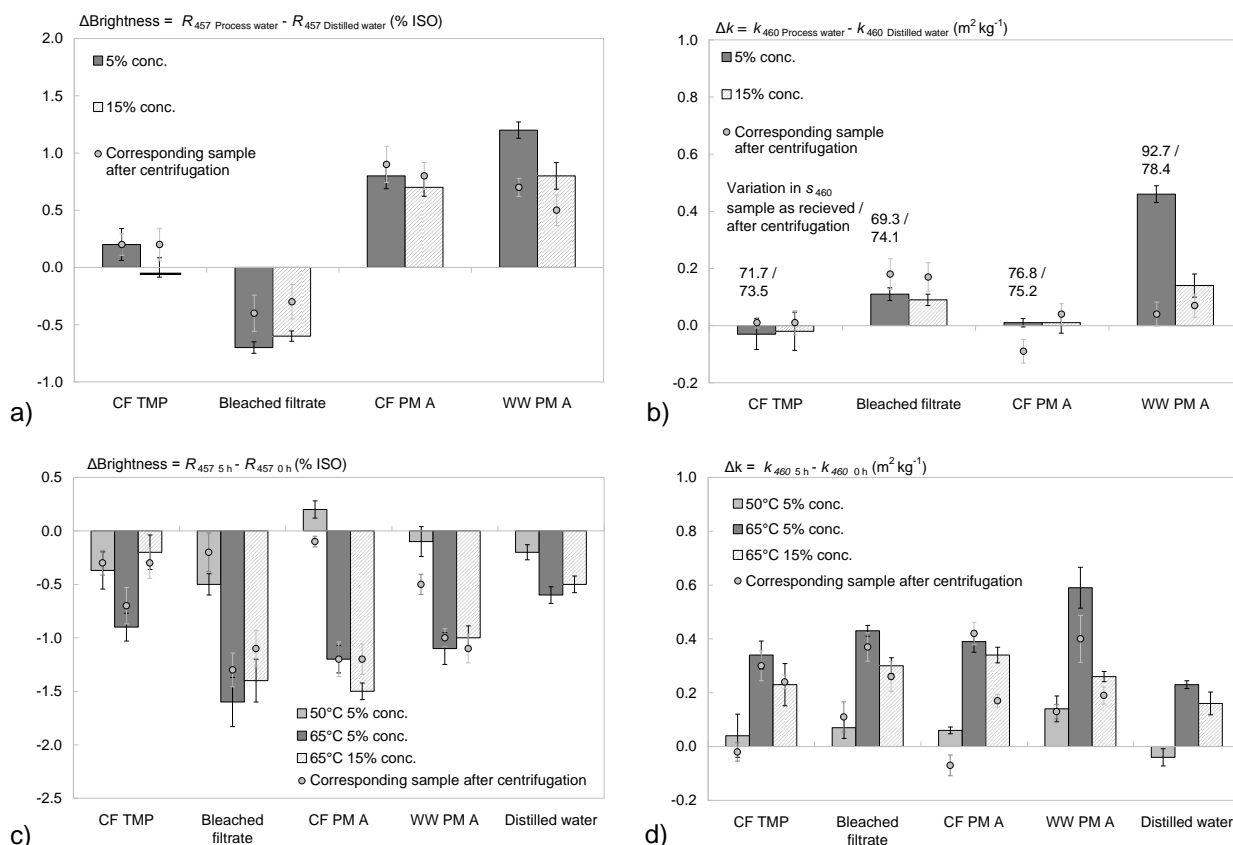
Fig 1 a-d - Change in ISO brightness and k_{460} upon dilution and/or storage of a well-washed hydrogen-peroxide bleached Norway spruce mechanical pulp stored in different waters for 5 hours with a 5% or 15% pulp consistency at 50°C or 65°C. The bars represent results for waters as received and the dots represent results for the corresponding sample after centrifugation. The error bars show the standard deviation of the optical measurements. a) The brightness of the pulp in process waters as compared to in distilled water at the time 0 hour. b) The light absorption coefficient (k) at 460 nm of the pulp in process waters as compared to in distilled water at the time 0 hour. The variation of light scattering coefficient (s) included in the figure at 460 nm for the pulp stored at 5% pulp consistency. c) The change in ISO brightness upon storage. d) The change in light absorption coefficient (k) at 460 nm upon storage.

In general, there were small differences between waters "as received" or after centrifugation; though in most cases the increase in k_{460} was smaller when pulp was stored in centrifuged waters. The WW PM stored at 5% pulp consistency at 65 °C was the water where this difference was largest due to centrifugation. The WW PM was the process water that gave the largest increase in k_{460}. The WW PM had the highest brightness value of all waters both before and after storage but this was also the water that gave the highest increase in k_{460}. The brightness values after storage were quite similar for distilled water and CF PM even though the decrease in brightness was larger for CF PM.

Storage trials for longer periods of time were performed for all process waters except CF TMP (*Fig 2a and b*). The discolouration was also more pronounced after longer storage times when pulp was stored in any of the process waters compared to the case with distilled water, which gave the highest brightness and the lowest k_{460} at all times studied (solid line in *Fig 2*).

All process waters gave quite similar results when used with the well-washed pulp, and at any given time the largest difference in brightness value was less than about 1.5 units. WW PM was the process water that gave the highest increase in k_{460} after 5 hours of storage (*Fig 1d*),

this could also be seen in *Fig 2b*, but after longer times the other curves reached a similar level in k_{460} as the washed pulp stored in the other process waters (grey shaded area in *Fig 2b*).

As a means of comparison, an unwashed pulp was also stored in distilled water and in WW PM. The brightness values were on the same level as those of the washed pulp (*Fig 2a*). The k_{460}-values, as a measure of the formation of colour, showed differences between washed and unwashed pulp. After short storage times, i.e. 5 hours, the increase in k_{460} for the unwashed pulp in distilled water was similar to the increase for the washed pulp in distilled water. Though after longer storage times, the darkening of the unwashed pulp in distilled water became similar to that of the washed pulp stored in the process waters (open circles, broken line). When the unwashed pulp was stored in WW PM, the increase in k_{460} was the highest at all times studied (broken line), showing the most extensive colour formation. This darkening did not show up as a decrease in brightness due to an increase in s_{460} from 86.0 to 94.4 m^2 kg^{-1}. The reasons for the increase in s_{460} are not known, but it is unlikely to contribute to the s-value of the finished paper. The coloured groups formed will eventually influence the brightness and whiteness of the finished paper made from
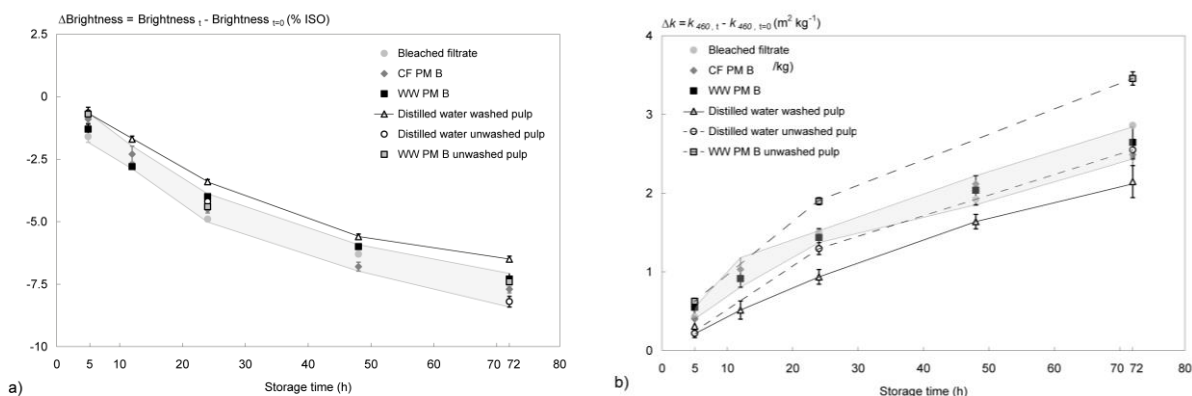
Fig 2 a-b - Change in ISO brightness and k_{460} during storage of unwashed or well-washed hydrogen-peroxide bleached Norway spruce mechanical pulp stored in different waters for 5–72 h at 5% pulp consistency and at 65°C. The error bars show the standard deviation of the optical measurements. a) The change in ISO brightness upon storage. b) The change in light absorption coefficient (k) at 460 nm upon storage. The lines and shaded areas are a guide to the eye.

this pulp. Furthermore, this difference indicates the importance of the cleanliness of pulp for avoiding the formation of colour during storage, both in distilled water and in process water.

It has been shown that the presence of clay, as in the WW PM samples, may be a major reason for the discolouration of pulp. In a study by Narvestad et al. (2013a) the "accessible iron" was proposed to cause the clay-induced discolouration. Different clays were stored together with DTPA, after which the iron content was measured in the water phase after centrifugation and filtration, and this iron content was defined as the accessible iron. The accessible iron constituted up to ~30% of the total iron content in the clay. The WW PM B sample in this investigation was stored together with an excess of DTPA in order to estimate which amount of the possible 20 mg L^{-1} was accessible. The iron content of the filtered water phase accessible iron was found to be 1.9 mg L^{-1}, which is the same as before the DTPA treatment. This means that the DTPA could not solubilise the iron present in the sample. In the study by Narvestad et al. (2013a), fresh clay was used in the experiments, whereas in the present study the filler had been circulated in the white water for a period of time so the accessible iron may have been dissolved into the water during the circulation. Nevertheless, the WW PM gave high k_{460}-values after 5 hours of storage, both as received and after centrifugation.

Fig 3 shows the influence of pH during storage of pulp in distilled water or process waters WW PM or CF PM. The decrease in brightness was less when pulp was stored in distilled water compared to when it was stored in process waters (1–1.5 units compared to 2–3 units. WW PM and CF PM showed similar results and are therefore represented by one solid curve. All waters were sensitive towards changes in pH and showed the lowest decrease in brightness at a pH of around 5.5–6.0, also shown as a minimum in Δk_{460}. These results are supported by the results presented by Narvestad et al. (2011) where hydrogen-peroxide bleached TMP was stored at 4% pulp

consistency for 5 hours in distilled water or clear filtrate from the paper machine, CF PM, at various pHs. Though in their study the brightness loss was the least when pH was somewhat lower (5.0–5.5), the brightness loss at this pH interval was ~1 unit when pulp was stored in distilled water and ~1.5 units when pulp was stored in clear filtrate from the paper machine. The increase in the light absorption coefficient at 460 nm showed the same relation to pH as the decrease in brightness. The smallest increase in k_{460} was seen at pH 5.5–6.0, and was lower when pulp was stored in distilled water compared to when it was stored in process waters. In a study by Gellerstedt et al. (1983), a minimum in relative colour formation, measured as $\Delta k/k_0 = (k_a–k_0)/k_0$ at 457 nm, where "0" is before treatment and "a" is after treatment, was seen at pH 5.5.

Fig 4a shows the light absorption coefficient (k_λ over the visible spectrum for pulp stored in the different waters. The values below 450 nm were considered unreliable as the light absorption was too strong (see e.g. Rundlöf et al. 1997; Karlsson et al. 2012). Therefore, these values were rejected.

The WW PM gave a broad shoulder in the absorption spectrum around 550–650 nm, which was present for both sampling occasions, A and B. There were no shoulders in the absorption spectra for any of the other process waters or distilled water, these showed a smooth increase in k with decreasing wavelength. The shoulder in the absorption spectra of WW PM could not be seen after centrifugation of the white water (broken line small steps), which shows that the shoulder in absorption spectra was related to particles which were removed by the centrifugation. In this case filler clay was probably involved (cf. *Table 1*). This shoulder in absorption spectra occurs in the same wavelength region where the added dyes have their absorption maxima (*Fig 4a*), which strongly indicates that this shoulder in absorption spectra was partly caused by added dyes adsorbed onto solid particles such as filler clay.
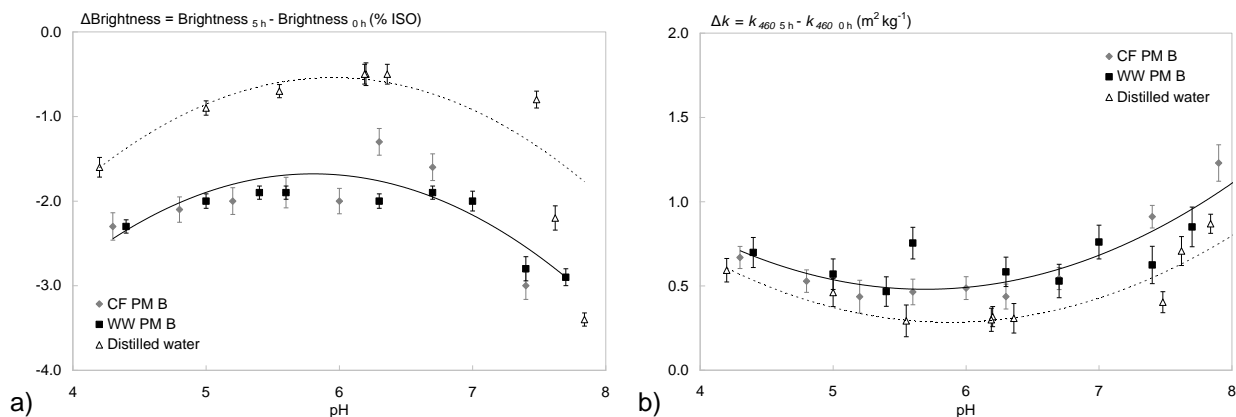
Fig 3 a-b - The influence of pH during storage of well-washed hydrogen-peroxide bleached Norway spruce mechanical pulp stored in different waters for 5 hours at 5% pulp consistency at 65°C. The error bars show the standard deviation of the optical measurements. a) The change in ISO brightness upon storage. b) The change in light absorption coefficient (k) at 460 nm upon storage.
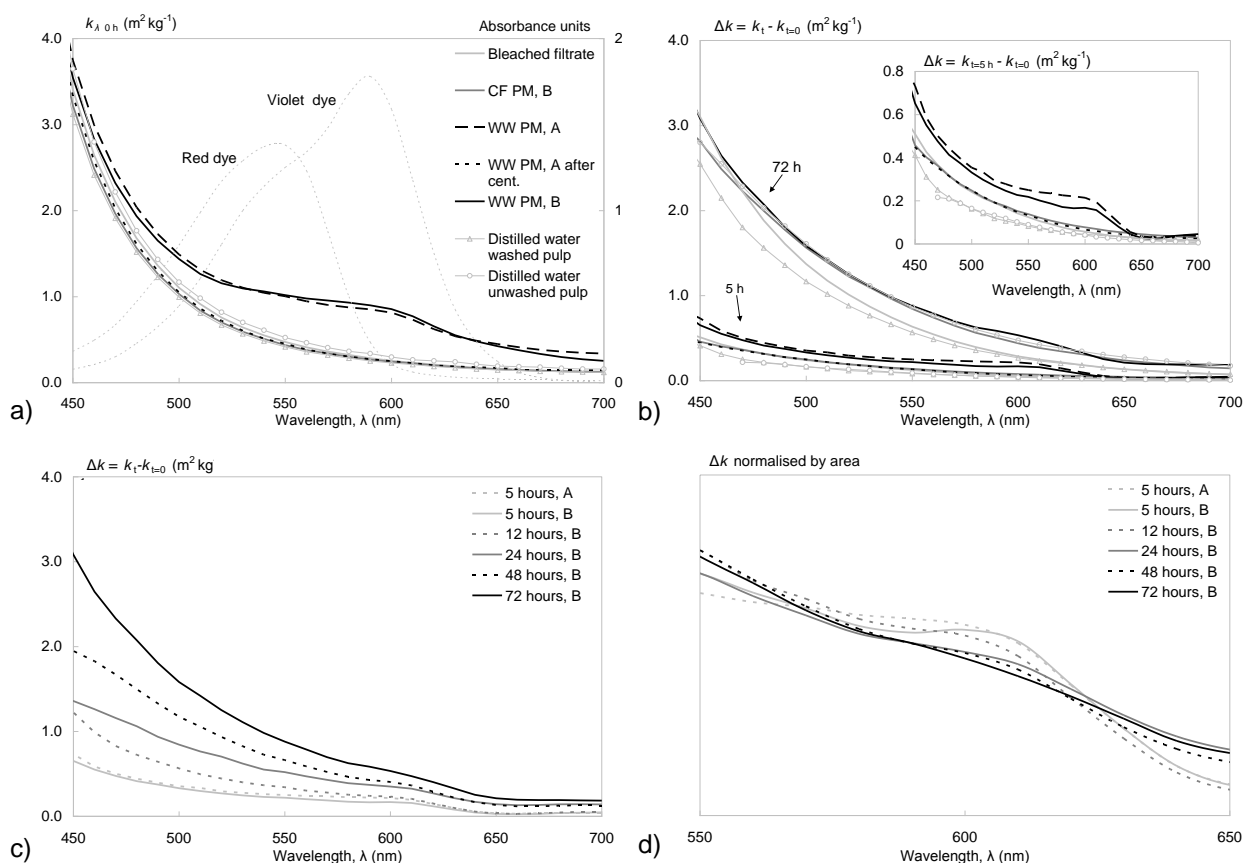

Fig 4 a-d - Spectral data for unwashed or well-washed hydrogen-peroxide bleached Norway spruce mechanical pulp upon dilution and/or storage in different waters. The WW PM was taken out on two different occasions marked A and B, data is also shown for WW PM after centrifugation. a) The light absorption coefficient over the visible spectra for pulp diluted to 5% consistency with different waters. On the secondary y-axis the absorbance spectra of the red and the violet dyes are shown. b) The difference spectra (k_{stored}-$k_{unstored}$) for pulp stored in different waters at 5% pulp consistency at 65°C for 5 hours and 72 hours. The legends are the same as for 4a. The smaller picture within the figure shows storage for 5 hours with a different scale on the y-axis. c) The difference spectra (k_{stored}-$k_{unstored}$) for pulp stored in WW PM (as received) at 5% pulp consistency at 65°C for 5, 12, 24, 48 and 72 hours. d) The curves in Figure 4c were normalised by the area, by dividing each value on a cure with the area under the same curve in the interval 550–650 nm.
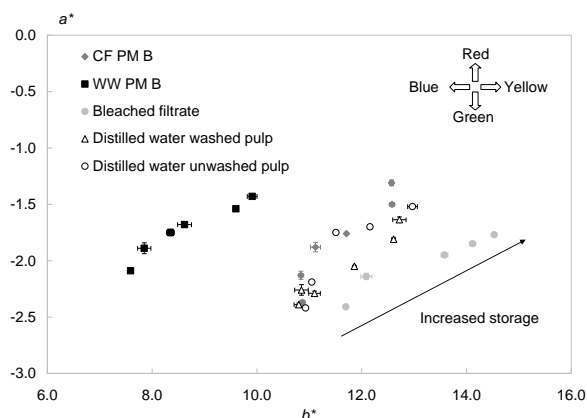
Fig 5 - The colour co-ordinates *a** and *b** for unwashed or well-washed hydrogen-peroxide bleached Norway spruce mechanical pulp stored in different waters for 5–72 hours at 5% pulp consistency at 65°C. The error bars show the standard deviation of the optical measurements.

Fig 4b shows the change in the light absorption coefficient during storage for all the waters shown in *Fig 4a* at two different storage times – 5 and 72 h. Within the figure, the increase in *k* after 5 hours of storage is shown as an inset with a magnified scale on the y-axis. The shoulder in absorption spectra at 550–650 nm was also present in the difference spectra ($k_{stored}-k_{unstored}$) of WW PM, which shows that additional colour was formed at these wavelengths during storage. From mill experience there is nothing supporting the fact that the dyes themselves should darken during storage.

For all waters there was a general increase in *k* with storage time, and the process waters showed a higher increase in *k* than the distilled water. In *Fig 4c*, the difference spectra of WW PM for all storage times studied are shown. As can be seen in the figure, the shoulder in absorption spectra at 550–650 nm was present at all storage times. The light absorption coefficient increased with storage time over the whole wavelength region studied. For short storage times the increase in *k* was most distinct at short wavelengths. Though, after storage over longer periods of time, the increase in *k* became noticeable over the whole spectrum, also at longer wavelengths.

To evaluate the relative importance of the *k*-values in the wavelength region of the shoulder at every storage time, each curve was normalised by area; each value on a curve was divided by the area under this curve in the wavelength interval 550–650 nm (*Fig 4d*). For short storage times, *k*-values around 600 nm represent a larger part of that curve, whereas for longer storage times, *k*-values around 600 nm are not more important compared to *k*-values at other wavelengths. This means that for short times the darkening, measured as an increase in *k,* was especially pronounced around ~600 nm, whereas for long storage times there was a more general darkening in the interval 550–650 nm.

It can be concluded that this shoulder in absorption spectra affects the reflectance of the pulp, as there was an obvious visible difference. Added dyes are partly the cause of this shoulder, as seen in *Fig 4a*, but probably not

the only cause because the shoulder in absorption spectra becomes stronger during storage (*Fig 4b–d*). Darkening of this type of dyes (i.e. cationic basic dyes) with time has not been reported to our knowledge, rather the opposite; Liu et al. (2007) reported that the maximum absorbance of a cationic basic dye decreased with increasing temperature in the range 20–50°C. *Fig 4b–d* indicate that some other chromophores absorbing light in the same region were formed during storage. Any detailed characterisation of chromophores is beyond the scope of this work. However, the shoulder in absorption spectra at 550–650 nm coincides with some absorption maxima of complexes between ferric (Fe^{3+}) ions and lignin or extractive model compounds reported in the literature: Polcin and Rapson (1972) reported an absorption maximum of 550 nm for a complex between Fe^{3+} and D-catechin; Friman et al. (2004) reported an absorption maximum of 565 nm for a complex between Fe^{3+} and tannin; Gosh and Ni (1998) reported an absorption maximum of ~590 nm for a complex between Fe^{3+} and catechol; Gore and Newman (1964) reported absorption maxima of ~500–600 nm for complexes between Fe^{3+} and a range of different phenols. Moldenius (1983) also saw an absorption maximum at 585 nm when ferric sulfate was added to a hydrogen-peroxide bleached groundwood pulp, which was probably due to the ferric-phenol complex with maxima at 590 nm. The absorption bands of all the complexes named above are broad, in most cases over the whole visible spectrum, and broad absorption maxima are seen. The sholder present in the spectrum for WW PM will be further studied in a forthcoming paper.

Fig 5 shows the colour co-ordinates CIE *a** and *b**. All experiments gave a change in colour towards red and yellow as storage time increased, initially more towards red and then more towards yellow. This corresponds with previous experiments (Enberg et al. 2013). This way of representing changes in colour also shows that the discolouration begins at shorter wavelengths and then gradually becomes noticeable at longer wavelengths (cf. *Fig 4b–d*). It is obvious that the starting point was quite different when white water from the paper machine, WW PM, was used. This was most probably due to the added dyes, as mentioned above. The shift towards red was more pronounced for CF PM compared to the other waters. The *L** values decreased with storage time in a similar way for all process waters, 2.0–2.7 units after 72 h, and are not included here.

Conclusions

For all process waters, the discolouration was more pronounced when the pulp was stored in process water compared to in distilled water. At 50°C the discolouration was small or negligible, but when increasing the temperature to 65°C the discolouration increased as expected. For all waters, the increase in k_{460} was less when the pulp was stored at a higher consistency, 15% compared to 5%. In general there were small differences between waters "as received" and after centrifugation, although in most cases the increase in k_{460} was smaller when pulp was stored in centrifuged waters. The white

water from the paper machine was the process water that gave the highest increase in k_{460} after 5 hours of storage, but after longer storage times the increase in k_{460} was quite similar for all process waters studied. The waters were sensitive towards changes in pH and showed the lowest decrease in brightness and a corresponding minimum in Δk_{460} at a pH around 5.5–6.0. The white water and clear filtrate from the paper machine showed similar results with a brightness decrease of 2–3 units, whereas storage in distilled water decreased the brightness less, by 1–1.5 units. The white water from the paper machine gave a broad shoulder in the light absorption spectrum around 550–650 nm, and the shoulder in absorption spectra was also present in the difference spectra (k_{stored}–$k_{unstored}$), which indicates that additional colour was formed at these wavelengths during storage. The shoulder in the absorption spectra for the white water from the paper machine could not be seen after centrifugation, which shows that the shoulder in absorption spectra was related to particles which were removable by centrifugation. The absorption maxima of the added dyes occur in the same wavelength region as the shoulder in absorption spectra and are partly, but probably not only, the cause of it as the shoulder becomes stronger during storage. The shoulder in absorption spectra at 550–650 nm coincides with some absorption maxima of complexes between ferric ions and lignin or extractive model compounds reported in the literature. The additional darkening may be caused by the formation of some of these chromohphores. There were no shoulders in the absorption spectra of any of the other process waters or distilled water, these showed a smooth increase in k with decreasing wavelength. CIE L^*, a^*, b^* data showed that the storage changed the colour of the pulp towards red and yellow, initially more towards red and then more towards yellow.

The washing of pulp before storage seems to be an influencing factor, storage of unwashed pulp in similar experiments gave higher k_{460}-values both in distilled water and in white water from the paper machine. The difference between unwashed and washed pulp is at least as large as the difference between using distilled water or process water in these initial experiments.

Acknowledgements

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