

This paper is published in the open archive of Mid Sweden University
DIVA <http://miun.diva-portal.org>
with permission of the publisher

Citation for the peer-reviewed published paper:

Fjellström H, Höglund H, Paulsson M. Light-induced yellowing of mechanical and chemimechanical pulp sheets : influence of wood raw material, process and ageing method. ; Nordic Pulp & Paper Research Journal. 2007;22(1):117-123.

URL to article at publishers site:

<http://dx.doi.org/10.3183/10.3183/NPPRJ-2007-22-01-p117-123>

Light-induced yellowing of mechanical and chemimechanical pulp sheets – influence of wood raw material, process and aging method

Helena Fjellström and Hans Höglund, Fibre Science and Communication Network (FSCN), Mid Sweden University, Sundsvall Sweden, Magnus Paulsson, Eka Chemicals AB, Bohus, Sweden

KEYWORDS: High-yield pulp, Softwood, Hardwood, Light-induced, Ageing, Light sources, Lignin, Pulping processes

SUMMARY: The light-induced brightness reversion of different types of unbleached and bleached high-yield pulps was studied under both accelerated and long-term ambient light-induced ageing conditions. It was found that accelerated ageing conditions that mimic indoor daylight exposures overestimate the yellowing tendencies of hardwood high-yield pulps (especially aspen pulps) compared to long-term ambient aging with no indirect sunlight present. It was, however, possible to predict the yellowing characteristics of softwood high-yield pulps. The lignin content of the pulps was found to be strongly correlated with the degree of photo-yellowing in the case of long-term ambient light-induced ageing. The presence of small amounts of birch chemithermomechanical pulp (CTMP) in a fine paper furnish resulted in extensive light-induced discoloration. The extent of photo-yellowing was found to be nearly linearly related to the amount of birch CTMP in the paper.

ADDRESSES OF THE AUTHORS: Helena Fjellström (helena.fjellstrom@miun.se) and Hans Höglund (hans.hoglund@miun.se): Mid Sweden University, Department of Natural Science, Holmgatan 10, SE-851 70 Sundsvall, Sweden. Magnus Paulsson (magnus.paulsson@eka.com): Eka Chemicals AB, SE-445 80 Bohus, Sweden.
Corresponding author: Helena Fjellström

With modern production technologies, high-yield pulps can be produced with mechanical and optical properties that render them suitable to be the major constituents of many grades of paper. Mechanical and chemimechanical pulps have many advantages, such as high yield and bulk, good printing properties, high light scattering ability and opacity, all of which make it possible to lower the basis weight of the produced paper. This, together with the fact that mechanical and chemimechanical pulps have less impact on the environment and can be produced with lower capital costs than chemical pulps, makes the use of high-yield pulps both an economically attractive and environmentally friendly way of using the world's wood resources.

The rapid brightness reversion (yellowing) that occurs upon exposure to daylight or indoor illumination is the major drawback hindering mechanical or chemimechanical pulps from being used in high-quality long-life paper products. It is generally accepted that it is the lignin constituent that is responsible for the brightness reversion that occurs, when paper is subjected to sunlight or indoor illumination containing UV radiation. The lignin forms compounds, chromophores, which absorb light in the blue-green region and turn the paper yellowish. Detailed information about the mechanism of yellowing and proposed stabilization methods can be found elsewhere

(Gratzl 1985; Heitner 1993; Leary 1994; Davidson 1996; Forsskåhl 2000; Lanzalunga, Bietti 2000). It is thus important to choose a pulp that is as photo-stable as possible if mechanical or chemimechanical pulps are to be used as the major constituents of high-quality grades of paper (e.g., fine papers). Brightness stability has been reported to differ depending on the wood species and mechanical pulp processes employed (e.g., Janson, Forsskåhl 1989; Johnson 1989, 1991; Agnemo et al. 1991; Paulsson, Ragauskas 2000). However, one problem encountered when determining the yellowing tendencies of lignin-containing materials is the lack of well-established testing procedures. A number of articles have examined the matter of brightness reversion and photo-yellowing, but it is difficult to compare the results of different studies, as most researchers have used their own ageing methods (cf. e.g., Johnson 1989; Bond et al. 1999, 2001; McGarry et al. 2003, 2004; Agarwal 2005). Different exposure conditions (humidity, temperature, etc.), light sources (light intensity, spectral distribution, etc.), exposure times, grammages of the exposed samples and procedures chosen for quantifying the colour reversion greatly influence the experimental outcome. Several investigations have shown that the spectral features of the light source used in photo-yellowing studies are of utmost importance (Paulsson, Ragauskas 1998; Paulsson et al. 2002; McGarry et al. 2004). Obviously, one must use a light source that produces light resembling, as closely as possible, that of the actual reversion situation, to obtain realistic accelerated ageing conditions and thereby relevant ageing results.

The present study describes the brightness reversion characteristics of a broad range of unbleached and bleached, mechanical and chemimechanical pulps produced from softwood or hardwoods on a commercial or pilot plant scale. Pulps bleached with oxidizing as well as reducing methods are included in the study. The chemistry of the reactions causing brightness reversion is not discussed in this paper, but has been reported in many other publications (cf. Heitner 1993; Leary 1994; Forsskåhl 2000; Lanzalunga, Bietti 2000). The effect of different amounts of birch chemithermomechanical pulp (CTMP) in a fine paper furnish will also be examined in more detail. The evaluation performed in this study was made using both long-term ambient and accelerated light-induced ageing.

Materials and Methods

Pulp samples

High-yield pulps, produced on a commercial or pilot plant scale, were used as received for the experiments

described in this work. The unbleached and bleached (with dithionite and/or hydrogen peroxide) mechanical or chemimechanical pulps were produced from both softwoods (mainly spruce) and hardwoods (aspen or birch). Commercially produced elemental chlorine free (ECF) bleached birch kraft pulp was used as a reference in the photo-ageing studies.

Preparation of paper sheets

Hand-made sheets with a grammage of 60 g/m² were prepared according to the SCAN CM 64:00 test method. The paper sheets were conditioned at 23°C and 50% relative humidity before being subjected to either ambient or accelerated light-induced ageing.

Paper sheets (fine paper type) with a grammage of 70 g/m² were produced on a small experimental paper machine (XPM, MoRe, Örnköldsvik, Sweden) with a head box width of 0.225 m and a machine speed of 0.5–3.0 m/min. The fibre furnish consisted of an ECF-bleached (chlorine dioxide/peroxide) softwood (spruce/pine) kraft pulp, an ECF-bleached (chlorine dioxide/peroxide/ozone) hardwood (birch) kraft pulp and a birch chemithermomechanical pulp (CTMP, 2% NaOH, 3% Na₂SO₃) in various admixtures. The filler (Syndcarb F0474-MJ, PCC; Omya AB) content of the paper sheets was 20%. The Hydrocol system (Hydrocol 878, 0.01%; Hydrocol SH, 0.06%, Ciba Specialty Chemicals) was used as the retention system, and as internal size ASA (Kemsize 200, 0.08%, Sellukem). The starch for the wet-end (Raiso R142, 0.50%; Raiso Chemicals) was split. 0.3% was added to the stock and 0.2% to the ASA. The produced papers were surface sized (C*size 05962, 2.86%, Cerestar) and had an ISO brightness of 83–90%. The paper sheets were conditioned at 23°C and 50% relative humidity before being subjected to either ambient or accelerated light-induced ageing.

Accelerated light-induced ageing

The accelerated ageing of the paper samples was performed with a Xenotest 150 (Heraeus, Hanau, Germany) equipped with a xenon lamp and with filters (ultraviolet and window glass) that eliminate radiation of wavelengths below 310 nm. The temperature was kept close to room temperature by means of a cooling fan. An optical sensor, compensating for possible main voltage fluctuations and lamp ageing, controlled the irradiance. The irradiance in the UV-A region was approximately 40 W/m². The spectral characteristics of the transmitted light are similar to those of average indoor daylight (sunlight behind window glass, cf. Paulsson, Ragauskas 1998).

Long-term ambient light-induced ageing

Long-term ambient light-induced ageing was performed by keeping the paper samples in an office environment in which the samples were exposed to light from two Philips TLD 18W/29 warm white fluorescent light tubes placed approximately 0.8 m above the samples. The paper samples were exposed to light from the fluorescent lamps 10 h per day to simulate an office environment. No indirect sunlight reached the paper samples.

Chemical analyses

The pulps were extracted with dichloromethane according to the procedure described in SCAN-CM 49:03 to determine extractives. The lignin content was determined as the sum of acid-insoluble (Klason) and acid-soluble lignin (Dence 1992). Absorptivity values of 113 dm³/gcm (at 205 nm, hardwood pulps) and 128 dm³/gcm (205 nm, softwood pulps) were used for the determination of the acid-soluble lignin. The lignin content is given as a percentage of the dry weight of the pulp.

Optical measurements

ISO brightness, light scattering (s) and light absorption (k) coefficients were measured using an Elrepho SE 071 spectrophotometer (Lorentzen & Wettre) according to ISO standard methods 2470 and 9416, respectively.

Results and Discussion

Light-induced ageing methods

To assess the photo-ageing characteristics of different types of high-yield pulps, a series of hand-made sheets were produced and aged under both ambient and accelerated conditions. The ageing conditions were as follows:

- *Accelerated ageing*: The paper samples were exposed to light from a xenon lamp, which mimics indoor daylight. The proposed ISO standard (N 1692) recommends this type of setup (xenon lamp with suitable filters) for such testing. The spectral characteristics of the light source are given in Fig 1a.
- *Long-term ambient ageing*: The paper samples were exposed to light from fluorescent lamps (10 h per day) in an office environment. No indirect daylight reached the samples. The spectral characteristics of the light source are given in Fig 1b.

The chosen ageing methods differ greatly in terms of the amount of UV radiation present, the total light intensity reaching the exposed samples and the spectral distribution of the emitted light. The amount and intensity of UV radiation has been found to be very low in a normal office environment (e.g., Jordan, O'Neill 1991; McGarry et al. 2004). Furthermore, it has been proposed that it is safe to model indoor photo-yellowing using solely artificial light (e.g., fluorescent lamps), i.e., no indirect daylight is needed (McGarry et al. 2004). The fact that no daylight reached the paper samples in the long-term

Table 1. Abbreviations used in figures and text.

| Abbreviation | Explanation |
|--------------|-----------------------------------|
| GWP | Groundwood pulp |
| BGWP | Bleached GWP |
| TMP | Thermomechanical pulp |
| BTMP | Bleached TMP |
| CTMP | Chemithermomechanical pulp |
| BCTMP | Bleached CTMP |
| HTCTMP | High temperature CTMP |
| BHTCTMP | Bleached HTCTMP |
| APMP | Alkaline peroxide mechanical pulp |
| ECF | Elemental chlorine free |

ambient ageing setup should therefore not influence the results obtained when simulating an office environment. This facilitates the execution of an ambient light-induced ageing procedure.

Paper samples enclosed in a dark environment will lose a few brightness units when storing them for longer periods of time, see e.g., Paulsson et al. 2002. However, this effect is small in comparison with the effect of UV/VIS radiation studied in this paper.

Light-induced ageing of different types of high-yield pulps

Figs 2–7 show the brightness reversion of a large number of high-yield pulps that were aged according to the two procedures described above. The abbreviations used in the figures and text below are explained in Table 1. Table 2 presents information regarding the brightness, bleaching chemicals, and lignin and extractive contents before ageing of the pulps examined.

As expected, a bleached pulp loses more brightness units during light exposure than an unbleached pulp does (see Figs 2–7, cf. Forsskähl 2000). This is partly a consequence of the Kubelka–Munk relationship (brightness is not linearly related to the chromophore content) and partly a consequence of the generation of light-sensitive structures during lignin-retaining bleaching (Forsskähl 2000). Thus, it is only relevant to compare paper samples with approximately the same initial brightness. It is, however, easy to compare the photo-yellowing characteristics of different pulps in the same brightness range when presenting the results in the form used in Figs 2–7. Furthermore, it is of special interest to follow the change in brightness values as brightness is most frequently used among the optical properties in the paper industry when describing the appearance of the paper.

Figs 2 and 3 shows the extent of brightness reversion after 1 h and 4 h of accelerated ageing, respectively. It is evident that the rather intense ageing conditions cause a severe yellowing in a very short period of time on both hardwood and softwood pulps. However, these results imply that hardwood pulps are somewhat more photo-stable than softwood pulps, regardless as to the pulping process used. This is in agreement with previously reported results (cf. Janson, Forsskähl 1989; Johnson 1989; Paulsson; Ragauskas 2000). The difference is most prominent in the high-brightness range. Groundwood pulps seem to be somewhat more photo-stable than refiner mechanical pulps are, at least in the high-brightness range. The bleaching method (dithionite or peroxide) or pre-treatment procedure (sulphite or alkaline peroxide) did not influence the photo-stability in any decisive way.

Fig 4 shows the extent of brightness reversion after 24 h of accelerated ageing.

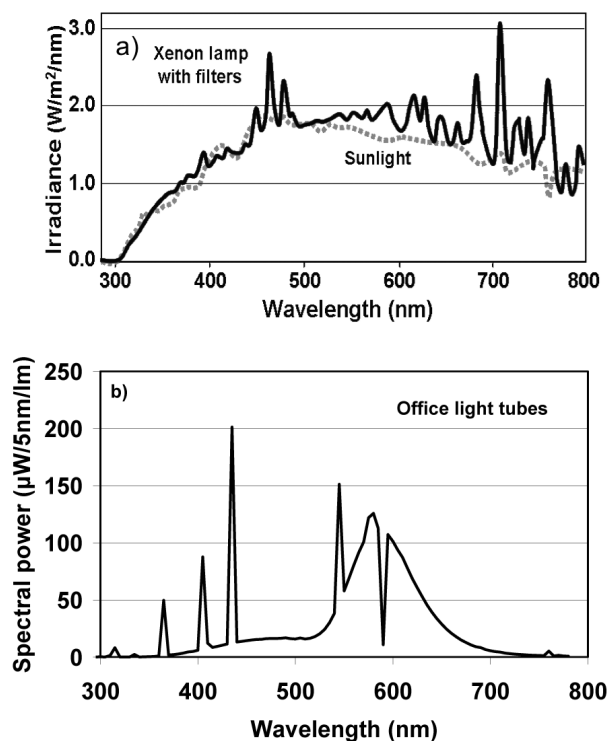


Fig 1. The spectral characteristics of the light sources used for the accelerated (a) and ambient (b) light-induced ageing procedures. The spectral energy distribution of sunlight is given in Fig 1a for the purposes of comparison.

Table 2. Pulp characteristics (brightness, bleaching chemicals, lignin and extractive contents) before ageing of the examined softwood and hardwood high-yield pulps. Some of the pulps were collected before their final bleaching.

| | Type of pulp ¹⁾ | Grade | Initial brightness (% ISO) | Bleaching chemicals | Total lignin content (%) ²⁾ | Acid-soluble lignin (%) | Extractives (%) |
|-------------------------------------|-------------------------------------|------------|----------------------------|---|--|-------------------------|-----------------|
| Spruce (<i>Picea abies</i>) | HTCTMP | Board | 58.4 | – | 26.8 | 0.2 | 0.2 |
| | TMP | LWC | 61.2 | – | 27.9 | 0.1 | 0.2 |
| | BTMP | News | 64.2 | Na ₂ S ₂ O ₄ | 27.1 | 0.1 | 0.1 |
| | BGWP | SC | 64.6 | Na ₂ S ₂ O ₄ | 28.0 | 0.1 | 0.2 |
| | BGWP ³⁾ | LWC | 73.4 | H ₂ O ₂ + Na ₂ S ₂ O ₄ | 28.4 | 0.2 | 0.1 |
| | BHTCTMP | Tissue | 74.0 | H ₂ O ₂ | 25.3 | 0.3 | 0.1 |
| | BGWP | SC | 74.5 | H ₂ O ₂ | 28.1 | 0.2 | 0.2 |
| | BTMP | LWC | 74.7 | H ₂ O ₂ | 27.8 | 0.2 | 0.1 |
| | BCTMP | Tissue | 75.8 | H ₂ O ₂ | 25.7 | 0.3 | 0.0 |
| | Birch (<i>Betula verucosa</i>) | CTMP | Board | 53.7 | – | 23.5 | 4.5 |
| CTMP | | Board | 62.4 | – | 21.7 | 4.6 | 0.2 |
| HTCTMP | | Board | 63.0 | Na ₂ S ₂ O ₄ | 23.0 | 4.9 | 0.3 |
| HTCTMP | | Board | 63.4 | – | 23.3 | 5.1 | 0.3 |
| BCTMP | | Board | 79.3 | H ₂ O ₂ | 21.6 | 4.6 | 0.1 |
| APMP ⁴⁾ | | Fine paper | 80.4 | H ₂ O ₂ | 21.1 | 6.4 | 0.1 |
| ECF | | | 85.0 | ClO ₂ + O ₂ | 0.0 | 0.0 | 0.1 |
| Aspen (<i>Populus tremula</i>) | CTMP | Fine paper | 65.7 | – | 24.4 | 2.6 | 0.3 |
| | BCTMP | Fine paper | 78.5 | H ₂ O ₂ | 22.2 | 3.3 | 0.1 |
| | BGWP | SC | 81.4 | H ₂ O ₂ | 21.3 | 3.0 | 0.2 |
| | APMP ⁴⁾ | Fine paper | 83.8 | H ₂ O ₂ | 21.0 | 4.4 | 0.1 |

1) For explanation of abbreviations, see Table 1

2) The total lignin content is the sum of Klason lignin and acid-soluble lignin

3) The pulp contains 66% spruce, 26% pine and 8% poplar

4) Alkaline hydrogen peroxide was used in the impregnation stages

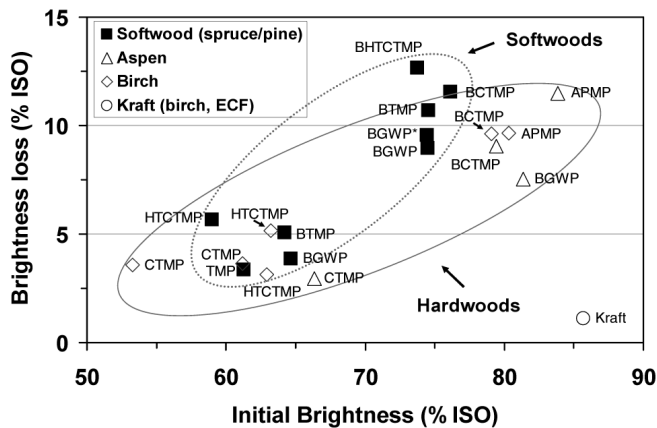


Fig 2. The change in ISO brightness after accelerated light-induced ageing for 1 h for different types of high-yield pulps. The ageing characteristics of an ECF-bleached birch kraft pulp are given as a reference. Abbreviations used in the figure can be found in Table 1. BGWP* contains 26% pine and 8% poplar; the rest is spruce.

Compared to the results presented in Figs 2 and 3, the results for the hardwood pulps have become somewhat more distinct from those for the softwood pulps, supporting the conclusion given above, i.e., that hardwood high-yield pulps are somewhat more photo-stable than softwood high-yield pulps are. To summarise, accelerated ageing for a longer period of time (24 h) did not change the general conclusions that were predicted after the shorter (1 h and 4 h) irradiation time.

Figs 5 and 6 shows the results of ambient light-induced ageing for 8 weeks and 20 weeks, respectively. It is evident that the hardwood pulps responded quite differently to the low-intensity ageing compared to how they responded to the light-induced accelerated ageing. The hardwood pulps were much more photo-stable throughout the 8 and 20-week ageing period, especially in the high-brightness range. This means that accelerated ageing performed as described above could overestimate the extent of brightness reversion of hardwood high-yield pulps. The ageing characteristics of the softwood pulps were, however, rather similar for the two ageing methods, regardless as to the high-yield pulping method employed (cf. Figs 2-3 and 5-6).

After one year of ambient light-induced ageing, it was apparent that the aspen pulps behaved differently (Fig 7). The brightness loss for aspen pulps, regardless as to the high-yield pulping process used, was much lower than the brightness loss experienced by softwood and birch pulps. Furthermore, the extent of yellowing of a birch pulp approaches that of a softwood pulp (see Fig 7), i.e., a birch high-yield pulp will only temporarily outperform a softwood high-yield pulp. Aspen-based mechanical or chemimechanical pulps should therefore be the preferred high-yield fibre source for long-life, high-quality paper grades. There is, however, one exception in the brightness range 60-85% ISO: birch APMP has a brightness loss similar to that of aspen pulps, probably because the APMP process has a somewhat lower yield than other mechanical pulping processes partly because more lignin is dissolved during processing (cf. Fig 9).

There can be several explanations of the observed differences between the softwood and hardwood pulps. Hardwoods contain less lignin (approximately 20–25% by dry weight) than do softwoods (approximately

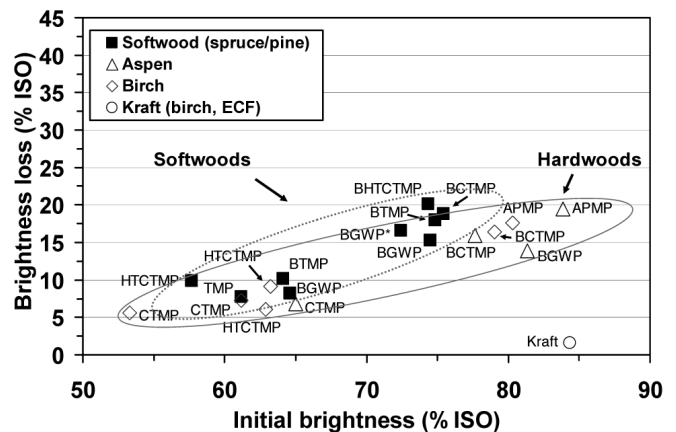


Fig 3. The change in ISO brightness after accelerated light-induced ageing for 4 h for different types of high-yield pulps. The ageing characteristics of an ECF-bleached birch kraft pulp are given as a reference. Abbreviations used in the figure can be found in Table 1. BGWP* contains 26% pine and 8% poplar; the rest is spruce.

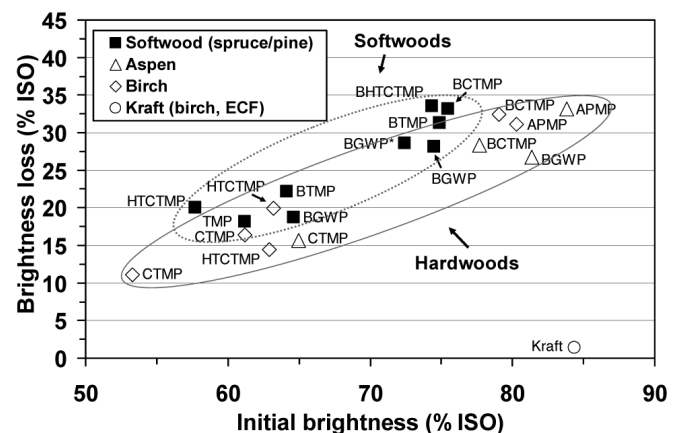


Fig 4. The change in ISO brightness after accelerated light-induced ageing for 24 h for different types of high-yield pulps. The ageing characteristics of an ECF-bleached birch kraft pulp are given as a reference. Abbreviations used in the figure can be found in Table 1. BGWP* contains 26% pine and 8% poplar; the rest is spruce.

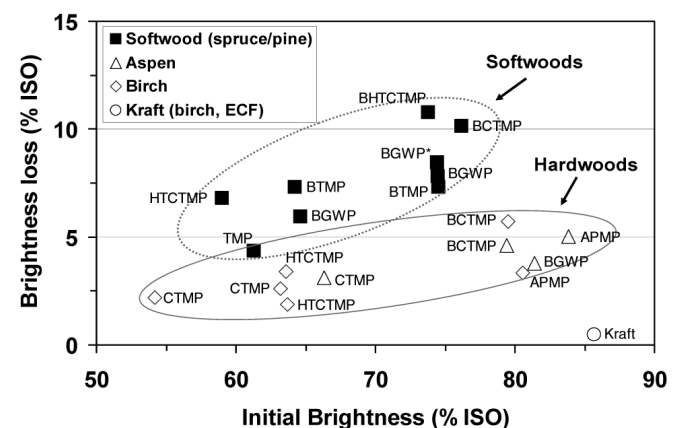


Fig 5. The change in ISO brightness after long-term ambient light-induced ageing for 8 weeks for different types of high-yield pulps. The ageing characteristics of an ECF-bleached birch kraft pulp are given as a reference. Abbreviations used in the figure can be found in Table 1. BGWP* contains 26% pine and 8% poplar; the rest is spruce.

26–32%); moreover, the lignin in hardwoods is syringyl/guaiacyl lignin, as opposed to the guaiacyl lignin in softwoods (Sjöström 1993). Lignin is an efficient absorber of UV radiation, and it is most likely the amount and structure of lignin influences the extent of absorption and thereby the photo-yellowing characteristics of a pulp. Variation in absorptivity in different

wavelength regions may not only influence the photo-yellowing tendency, but also the photo-bleaching ability of a high-yield pulp. Table 3 summarises the change in optical properties (ISO brightness, PC number) after accelerated and long-term ambient light-induced ageing for the high-yield pulps examined in this study.

Fig 8 shows the brightness loss of an aspen, a birch and a spruce chemithermomechanical pulp as a function of irradiation time for both the accelerated and ambient ageing conditions. The three hydrogen-peroxide-bleached pulps had about the same initial ISO brightness (76-79% ISO). It is well-known that the light-induced yellowing is characterised by a rapid initial phase followed by a slower less detrimental phase (cf. Lewis et al. 1945; Ek 1992). For the accelerated ageing conditions, the transition between the initial and secondary phase occurs somewhere between an irradiation time of 2-4 hours. It is interesting to notice that the initial phase for the low-intensity ambient ageing conditions is less pronounced and that the birch CTMP approaches the spruce CTMP after long-term ambient ageing. Fig 8 also shows that accelerated light-induced ageing for 4 h is comparable to long-term ambient light-induced ageing for about 20 weeks for the softwood pulp and 25-40 weeks for the hardwood pulps when the light-induced ageing is performed as described in the experimental section.

The relationship between lignin content and photo-yellowing in long-term aging

It is generally accepted that lignin is the main cause of the rapid light-induced yellowing of high-yield pulps. Since the accelerated ageing method was shown not to give reliable values for aspen pulps, the long-term ambient ageing method was chosen instead. Fig 9 shows the degree of photo-yellowing (measured as Δk_{457}) as a function of total lignin content in long-term ageing. It was evident that there exists a strong correlation between lignin content and the extent of photo-yellowing, regard-less as to the wood raw material, and pulping or bleaching method used.

Photo-yellowing of a fine paper containing various amounts of birch BCTMP

Fig 10 shows the brightness values before and after ambient light-induced ageing of papers containing various amounts of hydrogen peroxide-bleached birch CTMP. The degree of photo-yellowing was expressed as the post colour (PC) number at 457 nm (Giertz 1945). As can be seen in the figure, small amounts of birch BCTMP

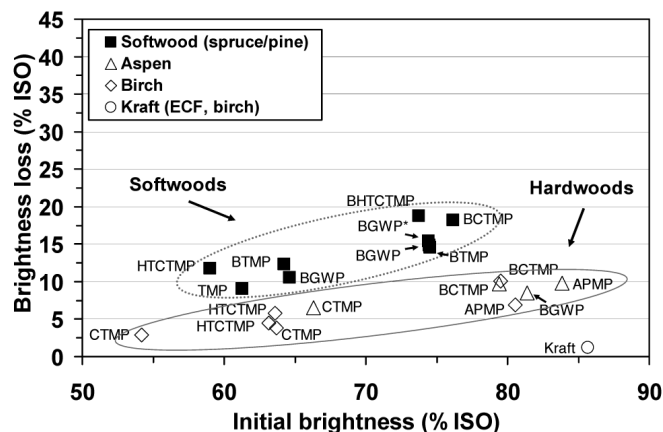


Fig 6. The change in ISO brightness after long-term ambient light-induced ageing for 20 weeks for different types of high-yield pulps. The ageing characteristics of an ECF-bleached birch kraft pulp are given as a reference. Abbreviations used in the figure can be found in Table 1. BGWP* contains 26% pine and 8% poplar; the rest is spruce.

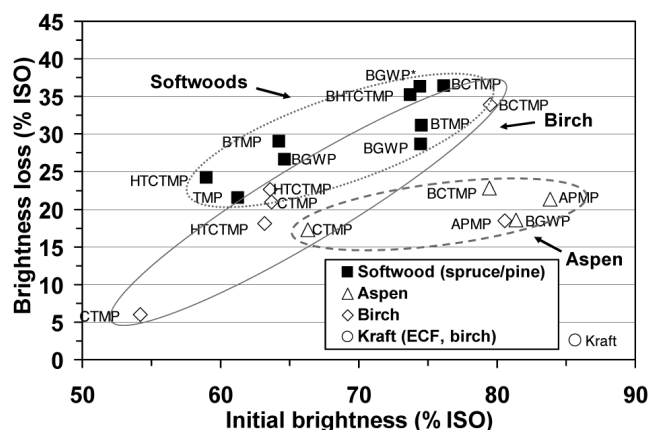


Fig 7. The change in ISO brightness after long-term light-induced ambient ageing for one year for different types of high-yield pulps. The ageing characteristics of an ECF-bleached birch kraft pulp are given as a reference. Abbreviations used in the figure can be found in Table 1. BGWP* contains 26% pine and 8% poplar; the rest is spruce.

Table 3. The change in optical properties of the examined softwood and hardwood high-yield pulps after accelerated and long-term ambient light-induced ageing. Corresponding changes for the birch kraft reference pulp is included for the purposes of comparison. The post colour (PC) number was calculated according to Giertz (1945).

| | Unaged Type of pulp | s (m ² /kg) | Accelerated, 1 hour | | Accelerated, 24 hours | | Office, 8 weeks | | Office, 52 weeks | |
|--|------------------------|---------------------------|-------------------------------|-----------|-------------------------------|-----------|-------------------------------|-----------|-------------------------------|-----------|
| | | | Δ Brightness (%ISO) | PC-number | Δ Brightness (%ISO) | PC-number | Δ Brightness (%ISO) | PC-number | Δ Brightness (%ISO) | PC-number |
| Spruce (<i>Picea abies</i>) | HTCTMP | 33.3 | 5.7 | 6.6 | 20.0 | 36.0 | 6.8 | 7.6 | 24.2 | 46.7 |
| | TMP | 57.4 | 3.4 | 3.1 | 18.2 | 25.5 | 4.4 | 4.1 | 21.5 | 33.3 |
| | BTMP | 53.9 | 5.1 | 4.1 | 22.2 | 30.1 | 7.3 | 6.4 | 29.0 | 49.6 |
| | BGWP | 77.1 | 3.9 | 3.0 | 18.7 | 22.1 | 5.9 | 4.9 | 26.6 | 40.8 |
| | BGWP ¹ | 73.0 | 9.6 | 5.7 | 28.6 | 30.8 | 8.4 | 4.4 | 36.4 | 45.9 |
| | BHTCTMP | 29.1 | 12.7 | 7.5 | 33.5 | 38.5 | 10.8 | 6.2 | 35.3 | 44.4 |
| | BGWP | 62.9 | 9.0 | 4.7 | 28.1 | 26.6 | 7.8 | 4.0 | 28.7 | 27.7 |
| | BTMP | 51.6 | 10.7 | 5.8 | 31.3 | 32.3 | 7.3 | 3.6 | 31.1 | 32.5 |
| BCTMP | 35.1 | 11.6 | 6.2 | 32.2 | 33.2 | 10.1 | 5.0 | 36.4 | 41.9 | |
| Birch (<i>Betula verucosa</i>) | CTMP | 41.9 | 3.6 | 5.0 | 11.1 | 19.1 | 2.2 | 2.8 | 6.0 | 8.6 |
| | CTMP | 43.2 | 3.7 | 3.4 | 16.4 | 21.7 | 1.9 | 1.4 | 20.9 | 28.0 |
| | HTCTMP | 43.5 | 3.1 | 2.6 | 14.4 | 16.4 | 2.6 | 2.1 | 18.1 | 22.7 |
| | HTCTMP | 35.7 | 5.2 | 4.5 | 20.0 | 26.6 | 3.4 | 2.7 | 22.6 | 32.0 |
| | BCTMP | 36.0 | 9.6 | 4.0 | 32.5 | 27.8 | 5.7 | 2.0 | 34.0 | 30.0 |
| | APMP | 30.2 | 9.7 | 3.7 | 31.1 | 23.7 | 3.3 | 1.0 | 18.5 | 9.2 |
| | ECF | 33.9 | 1.1 | 0.2 | 1.4 | 0.3 | 0.5 | 0.1 | 1.2 | 0.5 |
| Aspen (<i>Populus tremula</i>) | CTMP | 60.3 | 2.9 | 2.2 | 15.6 | 16.5 | 3.1 | 2.2 | 17.3 | 17.9 |
| | BCTMP | 49.4 | 9.1 | 4.0 | 28.3 | 22.8 | 4.6 | 1.6 | 22.8 | 14.0 |
| | BGWP | 68.9 | 7.5 | 2.5 | 26.7 | 16.7 | 3.8 | 1.1 | 18.6 | 8.9 |
| | APMP | 43.1 | 11.6 | 3.7 | 33.2 | 22.5 | 5.0 | 1.3 | 21.4 | 9.7 |

1) The pulp contains 66% spruce, 26% pine and 8% poplar

in the fine paper resulted in a severe brightness reversion. This is in agreement with previously reported results, where small amounts of hydrogen peroxide-bleached spruce CTMP or hydrogen-peroxide-bleached aspen CTMP were found strongly to decrease the photo-stability of papers containing an admixture of BCTMP and ECF-bleached kraft pulp (Paulsson, Parkås 2001; Paulsson et al. 2002; cf. also Johnson 1989). The degree of photo-yellowing was found to be nearly linear with respect to the amount of birch BCTMP in the paper.

Conclusions

The results presented here indicate that accelerated light-induced ageing that mimics the ageing occurring in average indoor daylight, overrates the yellowing tendencies of hardwood mechanical and chemimechanical pulps compared to softwood pulps, especially in the case of aspen high-yield pulps. Regardless as to the pulping or bleaching method used, a strong correlation between lignin content and the extent of long-term ambient photo-yellowing, was found. Small amounts of birch BCTMP in a fine paper furnish resulted in a severe brightness reversion.

It is evident that no matter how mechanical or chemimechanical pulps from a certain wood species are produced, they undergo similar photo-yellowing and lose brightness. The only difference is how rapidly the discoloration occurs. Hardwood high-yield pulps are more photo-stable (especially aspen pulps) and are therefore the first choice for fine paper applications. Based on this study, it is obvious that if lignin-containing pulps are to be used as major constituents of fine grades of paper, the brightness stability of such pulps has to be improved or the paper has to be protected.

Forthcoming work

Coating of the paper surface seems to be the most economical favourable way to protect the pulp from yellowing. The effect on brightness stability by coating layers on papers made from mechanical and chemimechanical hardwood pulps will be investigated in a forthcoming work where the effect of type and size distribution of different pigments in the coating colour will be studied in detail.

Acknowledgements

The authors would like to thank SCA Graphic Research AB, Sundsvall for valuable support. The Fibre Science and Communication Network (FSCN), EU Objective 1, the Region of South Forest Counties, The Knowledge Foundation and The Swedish Energy Agency are gratefully acknowledged for financial support.

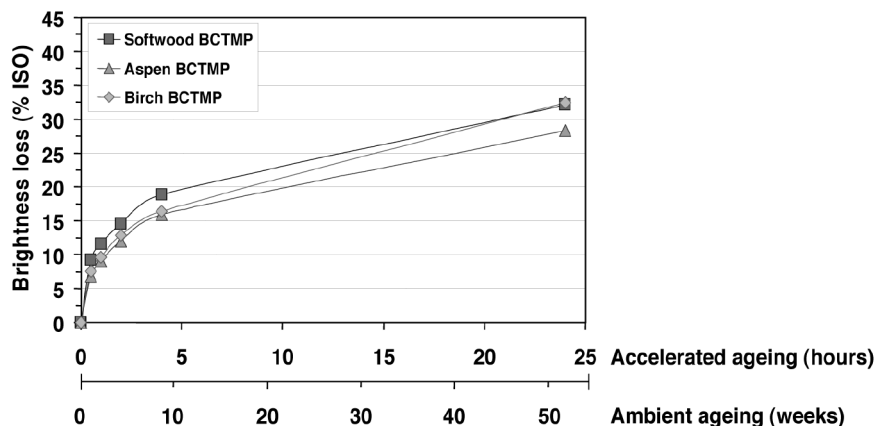


Fig 8. The change in ISO brightness after long-term ambient and accelerated light-induced ageing. Filled symbols represent accelerated ageing and unfilled symbols represent ambient ageing. The unaged brightness of the chemithermomechanical pulps was in the range of 76-79% ISO.

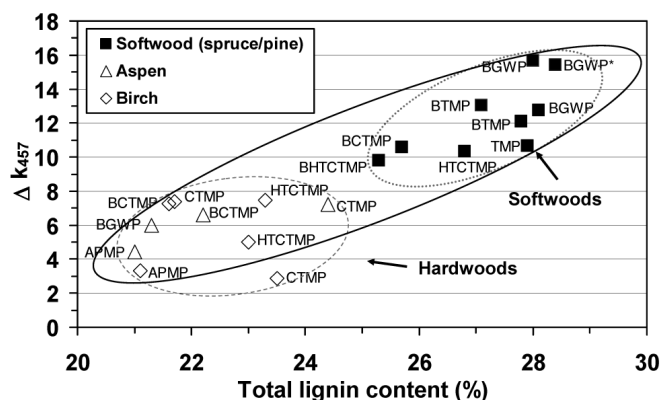


Fig 9. The extent of photo-yellowing (ΔK_{457}) after long-term light-induced ambient ageing for 1.5 years as a function of total lignin content (i.e., Klason lignin plus acid-soluble lignin) for various types of pulps. Abbreviations used in the figure can be found in Table 1. BGWP* contains 26% pine and 8% poplar; the rest is spruce.

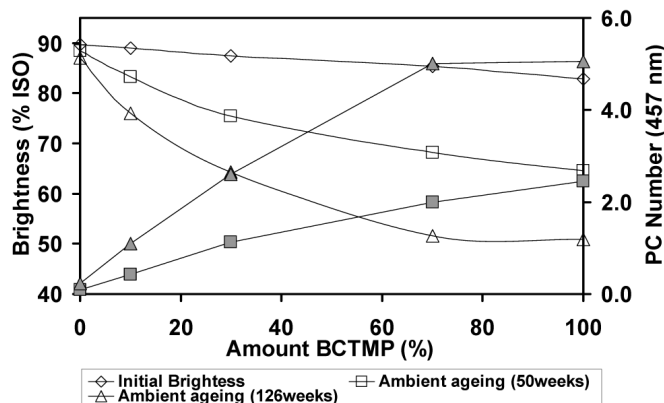


Fig 10. The change in ISO brightness (unfilled symbols) and PC number (filled symbols) as a function of the amount of birch BCTMP in the fine paper furnish. The papers were subjected to long-term ambient ageing for 50 and 126 weeks. The post colour (PC) number was calculated according to Gierzt (1945).

Literature

- Agarwal, U.P. (2005): Predicting photoyellowing behaviour of mechanical pulp containing papers, 13th Int. Symp. Wood Fib. Pulp. Chem., Auckland, New Zealand, May 16–19, 9–14.
- Agnemo, R., Francis, R.C., Alexander, T.C. and Dence, C.W. (1991): Studies on the mechanism of the photoyellowing of bleached mechanical and chemimechanical pulps. III. The role of hydroxyl radicals, *Holzforschung* 45(Suppl.), 101–108.
- Bond, J.S., Atalla, R.H., Agarwal U.P. and Hunt, C.G. (1999): The aging of lignin

rich papers upon exposure to light: Its quantification and prediction, 10th Int. Symp. Wood Pulp Chem., Yokohama, Japan, June 7–10, 500–504.

Bond, J.S., Yu, X., Agarwal U.P., Atalla, R.H. and Hunt, C.G. (2001): The aging of printing and writing papers upon exposure to light: Part 1 – Optical and chemical changes due to long-term light exposure, 11th Int. Symp. Wood Pulp. Chem., Nice, France, June 11–14, 209–213.

Davidson, R.S. (1996): The photodegradation of some naturally occurring polymers, *J. Photochem. Photobiol. B* 33(1), 3–25.

Dence, C.W. (1992): The determination of lignin. In: *Methods in Lignin Chemistry*. Edited by S.Y. Lin and C.W. Dence, Springer-Verlag, Berlin, Germany, pp. 33–61.

Ek, M. (1992): Some aspects on the mechanisms of photoyellowing of high-yield pulps, Ph.D. thesis, the Royal Institute of Technology, Stockholm, Sweden.

Forsskåhl, I. (2000): Brightness reversion. In: *Forest Products Chemistry*. Edited by P. Stenius, Fapet Oy, Helsinki, Finland, pp. 278–332.

Giertz, H.W. (1945): Om massans eftergulning, *Svensk Papperstidning*, 48(13), 317–323.

Gratz, J.S. (1985): Lichtinduzierte Vergilbung von Zellstoffen – Ursachen und Verhütung, *Papier* 39(10A), V14–23.

Heitner, C. (1993): Light-induced yellowing of wood-containing papers: An evolution of the mechanism. In: *Photochemistry of Lignocellulosic Materials*. Edited by C. Heitner and J.C. Scaiano, ACS Symposium Series 531, Washington, DC, USA, pp. 2–25.

Janson, J. and Forsskåhl, I. (1989): Colour changes in lignin-rich pulps on irradiation by light, *Nord. Pulp Paper Res. J.* 4(3), 197–205.

Johnson, R.W. (1989): Brightness stability of mechanical pulps: Relating laboratory data to performance, *Tappi J.* 72(12), 181–187.

Johnson, R.W. (1991): CTMP in fine papers: On-machine surface treatments for improved brightness stability, *Tappi J.* 74(5), 209–217.

Jordan, B.D. and O'Neill, M.A. (1991): The whiteness of paper: Colorimetry and visual ranking, *Tappi J.* 74(5), 93–101.

Lanzalunga, O. and Bietti, M. (2000): Photo- and radiation chemical induced degradation of lignin model compounds, *J. Photochem. Photobiol. B* 56(2–3), 85–108.

Leary, G.J. (1994): Recent progress in understanding and inhibiting the light-induced yellowing of mechanical pulps, *J. Pulp Paper Sci.* 20(6), J154–J160.

Lewis, H.F.; Reineck, E.A. and Fronmuller, D. (1945): The “fading” of groundwood by light. I. A study on the relation between the variables in sheet formation and fading, *Paper Trade J.* 121(8), 44–48.

McGarry, P.F., Schmidt, J.A. and Heitner, C. (2003): Accelerated aging of wood-containing papers is a poor predictor of end-use aging. 12th Int. Symp. Wood Pulp. Chem., Madison, WI, USA, June 9–12, 223–226.

McGarry, P.F., Schmidt, J. and Heitner, C. (2004): Accelerated light exposure of wood containing pulps. Part I: Effects of wavelength and intensity, *Tappi J.* 3(10), 18–24.

Paulsson, M. and Ragauskas, A.J. (1998): Chemical modification of lignin-rich paper. Part 8: Effect of light source on the accelerated light-induced yellowing of untreated and acetylated high-yield pulps, *Nord. Pulp Paper Res. J.* 13(2), 132–142.

Paulsson, M. and Ragauskas, A.J. (2000): Chemical modification of lignin-rich paper. Light-induced changes of softwood and hardwood chemithermomechanical pulps. The effect of irradiation source. In: *Lignin: Historical, Biological, and Material Perspectives*. Edited by W.G. Glasser, R.A. Northey and T.P. Schultz, ACS Symposium Series 742, Washington, DC, USA, pp. 490–504.

Paulsson, M. and Parkås, J. (2001): Long-term natural aging of untreated and chemically modified high-yield pulps, 11th Int. Symp. Wood Pulp. Chem., Nice, France, June 11–14, 227–230.

Paulsson, M., Parkås, J. and Ragauskas, A.J. (2002): Long-time natural aging of untreated and additive-treated aspen CTMP, 7th European Workshop on Lignocellulosics and Pulp, Åbo, Finland, August 26–29, 325–328.

Sjöström, E. (1993): *Wood Chemistry – Fundamentals and Applications*, Academic Press Inc., San Diego, CA, USA, pp. 71–89.

*Manuscript received April 5, 2006
Accepted November 20, 2006*