



## **INHIBITION OF LIGHT-INDUCED COLOUR REVERSION OF WOOD-CONTAINING PAPERS BY MEANS OF COATING**

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## **INHIBITION OF LIGHT-INDUCED COLOUR REVERSION OF WOOD-CONTAINING PAPERS BY MEANS OF COATING**

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## ABSTRACT

The main purpose of this thesis was to find ways to maintain a low level of light-induced discolouration at an increased addition of mechanical and chemimechanical pulps in coated high-quality fine paper and magazine paper grades. Current technology allows the production of high-yield pulps such as thermomechanical and chemimechanical pulps with properties suitable for manufacturing high-quality paper or paperboard with a low basis weight. Coating of wood-containing paper will probably be necessary for photo-stability reasons if lignin-containing pulps are to be used as the main fibre furnish in long-life and high-value products.

In order to find the most suitable pulp for this purpose, light-induced discolouration of a variety of paper samples from unbleached and bleached softwood and hardwood pulps was studied under both accelerated and long-term ambient light-induced ageing conditions. Hardwood high-yield pulps, especially aspen pulps, were proven to be more photo-stable compared to softwood pulps. Hardwood pulps should therefore be the first choice for applications where a high permanence is desirable. Evaluating ageing characteristics using the CIELAB colour system showed that accelerated ageing conditions tend to mainly increase the  $b^*$  value and decrease the  $L^*$  value (i.e. yellow the pulp), whereas long-term ambient ageing also increases the  $a^*$  value, which makes the pulp more reddish.

A new method for studying the influence of the UV-screening properties of coating layers on a base paper was developed, and used to investigate the effect of pigment, pigment size distribution, binder and UV-absorbing additives. The coat weight and pigment type were found to be the most important factors for reducing the transmittance of UV-radiation. Coating colours containing kaolin pigments had a lower UV-transmittance than calcium carbonate pigments. Of the calcium carbonates, precipitated calcium carbonates were better than ground calcium carbonates and the difference was greater at higher coat weights. The particle size

distribution should preferably be narrow. When the best pigment (bleached kaolin) and the best binder (styrene butadiene latex) were combined with titanium dioxide, the UV-transmittance could be reduced by about 90% at a coat weight of ~10 g/m<sup>2</sup>. At a coat weight close to 20 g/m<sup>2</sup>, the transmittance was close to zero. This shows that it is possible to more or less fully protect a double coated base paper from harmful UV-radiation, when the coating layer has an optimum composition for that purpose. A prerequisite to reach so far is that the coating layer has an even coat weight.

Keywords: High-yield pulp, CTMP, birch, light-induced, ageing, photo-stabilising, lignin, coating, pigment, kaolin, calcium carbonate, titanium dioxide, binder, FWA

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## LIST OF PAPERS

This thesis is based on the following five papers, which will be referred to by their Roman numerals:

- Paper I      **Light-induced yellowing of mechanical and chemimechanical pulp sheets: Influence of wood raw material, process and ageing method**  
FJELLSTRÖM, H., HÖGLUND, H. and PAULSSON, M.  
*Nordic Pulp and Paper Research Journal*, 22(1), 117–123, (2007), and  
*Nordic Pulp and Paper Research Journal*, 22(2), 275, (2007).
- Paper II      **Discolouration of mechanical and chemimechanical pulps: Influence of wood raw material, process and ageing method**  
FJELLSTRÖM, H., HÖGLUND, H., PAULSSON, M. and RUNDLÖF, M.  
Accepted for publication in *Nordic Pulp and Paper Research Journal*, 23(1), (2008).
- Paper III      **A novel method of studying the ability of a coating layer to retard the photoyellowing of the base paper**  
FJELLSTRÖM, H., HÖGLUND, H., FORSBERG, S., PAULSSON, M. and RUNDLÖF, M.  
*Nordic Pulp and Paper Research Journal*, 22(3), 343–349, (2007).
- Paper IV      **Inhibition of light-induced brightness reversion of high-yield pulps: The UV-screening properties of coating layers containing kaolin or calcium carbonate pigments**  
FJELLSTRÖM, H., HÖGLUND, H., FORSBERG, S. and PAULSSON, M.  
*Nordic Pulp and Paper Research Journal*, 22(3), 350–355, (2007).
- Paper V      **The UV-screening properties of coating layers: The influence of pigments, binders and additives**  
FJELLSTRÖM, H., HÖGLUND, H., FORSBERG, S. and PAULSSON, M.  
Submitted to *Nordic Pulp and Paper Research Journal* (2007).

## CONTRIBUTION REPORT

The author's contributions to the papers in this thesis are as follows:

- |           |   |
|-----------|---|
| Paper I   | Experimental work, interpreting the results and writing the article.  |
| Paper II  | Experimental work, interpreting the results and writing the article.  |
| Paper III | Experimental work, interpreting the results and writing the article.<br>The parts regarding the detailed description of UV-VIS spectroscopy measurements and determination of $s$ and $k$ were written by Mats Rundlöf. |
| Paper IV  | Experimental work, interpreting the results and writing the article.  |
| Paper V   | Experimental work, interpreting the results and writing the article.  |

## RELATED MATERIAL

Results related to this work were presented at international conferences:

### **Influence of coating formulation on light-induced brightness stability of mechanical and chemimechanical pulp sheets**

FJELLSTRÖM, H., HÖGLUND, H., PAULSSON, M. and FORSBERG, S.

Proceedings of *International Mechanical Pulping Conference, Oslo, Norway*, 339–343, (2005).

### **A novel method for studying the photo-stabilising properties of coating layers**

FJELLSTRÖM, H., HÖGLUND, H., FORSBERG, S. and PAULSSON, M.

Presented at the *5th Fundamental Mechanical Pulp Research Seminar, Trondheim, Norway*, (2006).

## 1. INTRODUCTION

Modern technologies allow the production of high-yield pulps (e.g. thermomechanical pulp, TMP and chemithermomechanical pulp, CTMP) with mechanical and optical properties that render them suitable for use in a variety of paper grades. Such papers have other advantages such as high yield and bulk, good printing properties and high opacity and light scattering ability, all of which make it possible to produce high quality paper or paperboard with a low basis weight. In addition, mechanical and chemimechanical pulps have less impact on the environment than chemical pulps, and can be produced in mills with lower capital costs. Hence, the use of high-yield pulps is both an economically attractive and an environmentally friendly way of using the world's wood resources. However, all these positive features are offset by inferior brightness stability. When paper from mechanical and chemimechanical pulps is subjected to ultraviolet radiation (present in daylight and indoor illumination), light-absorbing chromophores are formed, giving the paper a yellowish hue. This discolouration, which leads to a decrease in brightness and whiteness, is ascribed to the lignin component in the pulp.

Numerous investigations have been made to detect what type of chromophores that initially are formed, but the results are contradictory. There may be various explanations behind this discrepancy. Firstly, brightness stability of high-yield pulps have been reported to differ depending on the wood species used and the mechanical or chemimechanical pulp process employed for producing the pulp. It is also difficult to compare the results of different studies, since the lack of well-established testing procedures has led to most researchers using their own light-induced ageing methods. Different exposure conditions (humidity, temperature etc.) light sources (light intensity, spectral distribution etc.) exposure times and grammages of the exposed samples are of the utmost importance. The optical properties measured will also greatly influence the interpretation of the ageing characteristics of a pulp.

Over the years, there have been a number of efforts to inhibit or slow down the light-induced discolouration of lignocellulosic materials. Some of the approaches have been based on chemical modification of the reactive structures in lignin using reductive or oxidative treatments with the aim of suppressing the formation of chromophores. An alternative approach is to use additives of various types such as antioxidants, polymers and quenchers. However, none of these approaches have resulted in a cost-efficient, technically feasible and non-toxic solution to the problem.

Today, the differences in quality between different types of wood-containing and wood-free printing and writing paper grades have been reduced and more paper products are being coated to enhance the quality of print and images. Coating of paper has also the potential to retard light-induced discolouration, and

for photo-stability reasons is most likely necessary if pulps containing lignin are to be used as the main fibre furnish in long-life and high-value products. The extensive influence on photo-stability of factors such as pigment type, pigment size distribution, coat weight, binders, additives and the homogeneity of the coating layer are well known. It is therefore important to also examine the influence of pigment and binder type, and the particle size and distribution of commercial coating pigments, on the UV-screening properties of coating layers.

## **1.1 Objective**

The overall aim of this work was to find solutions to increase the usage of mechanical and chemimechanical pulps in high-quality paper grades where a low level of light-induced discolouration is important. One part of this objective was to find the most suitable high-yield pulp for this purpose. Another, was to investigate the effectiveness of the coating layers used in light weight coated (LWC), medium weight coated (MWC) or fine paper grades to hinder or slow down the light-induced discolouration, in order to find the best coating formulation in terms of pigment type, pigment size distribution, binder and UV-absorbing additives.

## **1.2 Contents description**

A short description of the contents of this thesis is given below:

The background of the research is presented in chapter 2. Sections 2.1-2.3 provide a short description of wood as raw material and mechanical and chemimechanical pulping processes, and this is followed by a discussion of the phenomenon of light-induced discolouration, and ways of inhibiting it (see sections 2.4 and 2.5).

The materials and methods used are briefly presented in chapter 3. The last section of this chapter (section 3.5) describes briefly a new method that was developed to study the reflectance/transmittance properties of thin coating layers in relation to their effect of light-induced discolouration.

The results of the investigations and related discussions are presented in chapter 4. Section 4.1 deals with light-induced discolouration of high-yield pulps, while section 4.2 describes the development of a new method for studying coating layers. Section 4.3 describes the influence of pigment type, pigment size distribution, binders and UV-absorbing additives on the UV-screening properties of coating layers.

Chapter 5 contains general discussions and comparisons of the new findings in relation to the objectives of this work.

Chapter 6 presents the conclusion of the research described in this thesis.

In chapter 7, some ideas for future work are presented.

## 2. BACKGROUND

*This chapter provides some background information in order to facilitate the interpretation of the results presented in the following chapters. The chapter starts with a short description of wood as raw material and mechanical and chemimechanical pulping processes. This is followed by a discussion of the phenomenon of light-induced discolouration, and ways of inhibiting it.*

### 2.1 Wood components

The section below is a short summary of the components in wood. More detailed information can be found in for example, Rydholm (1965), Fengel and Wegener (1989), Sjöström (1993), Back and Allen (2000) and Hon and Shiraishi (2001).

Wood cells consist mainly of cellulose, hemicelluloses, lignin, extractives, and inorganic material. The major component, cellulose, makes up 40–45% of the dry weight of wood. Cellulose is a linear homopolysaccharide composed of  $\beta$ -D-glucopyranose units linked together by (1 $\rightarrow$ 4)-glycosidic bonds.

Hemicelluloses (20–35% of the dry weight of the wood) are heterogeneous polysaccharides that are relatively easily hydrolysed to their monomeric components by acids. The monomeric components include D-glucose, D-mannose, D-galactose, D-xylose, L-arabinose, and small amounts of L-rhamnose in addition to D-glucuronic acid, 4-O-methyl-D-glucuronic acid and D-galacturonic acid. Some of the polysaccharides in hemicellulose are extensively branched. The composition and structure of the hemicelluloses in softwood differ from those in hardwood. The main hemicelluloses in softwood are galactoglucomannans (~20%), arabinoglucuronoxylans (7–10%) and arabinogalactans; while glucuronoxylans (15–30%) and glucomannans (2–5%) are the main hemicelluloses in hardwood.

Lignins are polymers of the phenylpropane units guaiacylpropane, syringylpropane and *p*-hydroxyphenylpropane. The main monomeric unit of softwood lignin is of the guaiacylpropane type, while hardwood lignin is a mixture of guaiacylpropane and syringylpropane units. In softwoods, lignin make up 27–30% of the dry weight of wood, while in hardwoods; they constitute only ~20%.

Extractives are compounds that are soluble in a neutral organic solvent or in water. They may be lipophilic or hydrophilic, and can be regarded as non-structural wood elements. Common extractives include fats, fatty acids, waxes, terpenoids, steroids, and phenolic constituents. The inorganic content in wood seldom exceeds 1% of the dry wood weight, and consists mainly of salts of calcium, potassium, and magnesium. The concentration of these components varies between hardwood and softwood, between different wood species, between different trees within the same wood species, and between different morphological regions within the same tree. Table 1 shows typical values for the chemical

composition and the fibre characteristics of the most common Scandinavian wood species.

**Table 1.** Typical chemical and morphological characteristics of Scandinavian wood species. The data in Table 1 were collected from Sjöström (1993), Rydholm (1965) and Vesterlind (2006). Data given as intervals are related to differences between earlywood and latewood fibres.

Wood raw material	Spruce ( <i>Picea abies</i> )	Pine ( <i>Pinus sylvestris</i> )	Birch ( <i>Betula verrucosa</i> )	Aspen ( <i>Populus tremuloides</i> )
Cellulose (%)	41.7	40.0	41.0	50
Hemicelluloses (%)	28.3 <sup>1)</sup>	28.5 <sup>1)</sup>	32.4 <sup>1)</sup>	30.5
Lignin (%)	27.4	27.7	22.0	16
Extractives (%)	1.7 <sup>2)</sup>	3.5 <sup>2)</sup>	3.2 <sup>2)</sup>	3 <sup>3)</sup>
Residual constituents(%)	0.9	0.3	1.4	0.5
Fibre length (mm)	35	35	12	10
Fibre thickness (mm)	20-35	20-35	20	18
Fibre wall thickness (mm)	2.3-4.5	2.3-4.5	3.7	2.0

1). Including glucomannan (+ galactose and acetyl in softwood), glucuronoxylan (+ arabinose in softwood and acetyl in hardwood) and other polysaccharides

2). CH<sub>2</sub>Cl<sub>2</sub> followed by C<sub>2</sub>H<sub>5</sub>OH.

3). Ethanol - benzene

## 2.2 Mechanical and chemimechanical pulping

Pulps from wood are produced by either mechanical or chemical means. The production of chemical pulp is based mainly on kraft (sulphate) or sulphite processes. In these processes, chemicals dissolve nearly all of the lignin and part of the hemicelluloses that were originally present in the wood chips. Compared to bleached chemical pulps, which generally have a yield of 45–50%, mechanical pulping gives a much higher yield, usually between 97–98%, because only a small amount of the lignin and hemicellulose are dissolved. When mechanical pulps are hydrogen peroxide bleached, an additional 3–6% of the lignin and hemicellulose are dissolved (Holmbom et al. 2005). Mechanical pulping also offers the advantage of a lower investment cost due to the simpler process design compared to chemical pulping.

The main types of mechanical pulps are thermomechanical pulp (TMP), groundwood pulp (GWP), and pressure groundwood (PGW) pulp. In TMP processing, wood chips are first preheated with pressurised steam to 130-150°C. Next, the heated chips and water are fed into a disc refiner where the fibres are separated (i.e., torn apart) as a result of an intense treatment in a small gap between rotating patterned discs, thus generating a pulp consisting of fibres and fine materials (Tienvieri et al. 1999). In chemithermomechanical pulping (CTMP),

the wood chips are not merely preheated ( $<140^{\circ}\text{C}$ ) but also have small amounts of chemicals, normally sodium sulphite and/or alkali, added at the pre-treatment in an impregnation stage. The pre-heating operation and the chemicals soften the lignin, which facilitates fibre separation and makes the fibre material more flexible (Lindholm, Kurdin 1999). The high temperature CTMP (HTCTMP) process is technically the same as the CTMP process; the only difference is the preheating and refining temperature which in the HTCTMP process is well above the softening temperature of lignin, i.e.  $>160^{\circ}\text{C}$ . Alkaline peroxide mechanical pulps (APMP) are produced by pre-treating wood chips with alkali and hydrogen peroxide, and then refining them normally under atmospheric conditions (Lindholm, Kurdin 1999). In production of groundwood pulps, the wood logs are not chopped into chips, but are pressed against a rotating grind stone under atmospheric (GWP) or steam pressurised (PGW) conditions. Through actions of grits in the surface of the stone, fibres are pulled out of the wood matrix (Liimatainen et al. 1999).

Papers produced from mechanical pulps are characterised by high bulk (low density), high opacity, high light-scattering ability and good printing properties. The high opacity and the high light-scattering ability are related to the high fines content, while the high bulk is related to the high bending stiffness of the fibres. The drawbacks of mechanical pulping, compared to chemical pulping, is the high electrical energy demand, the lower strength properties of the paper due to lower bonding capacity and less flexible fibres, and a high light-induced brightness reversion. If mechanical or chemimechanical pulps are to be used as the major constituents of high-quality grades of paper (e.g., fine paper, LWC or SC papers), it is important to choose a pulp that is as photo-stable as possible.

### **2.3 Bleaching of mechanical and chemimechanical pulps**

Bleaching of mechanical and chemimechanical pulps is performed with the purpose of improving their brightness, and can be completed in two ways; reductively or oxidatively. Reductive bleaching usually involves sodium dithionite ( $\text{Na}_2\text{S}_2\text{O}_4$ ) as bleaching chemical and is performed at pH 4.5-6.5 and a temperature of  $50\text{-}70^{\circ}\text{C}$ . In general, reductive bleaching is not enough to reach the highest brightness levels, since the brightness gain is about 10-12 ISO brightness units. With oxidative bleaching on the other hand, very high brightness levels can be gained, and brightness increases of more than 20 ISO brightness units is possible. The chemicals used in oxidative bleaching are normally hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), alkali, sodium silicate ( $\text{Na}_2\text{O} \times n\text{SiO}_2$ ) and chelating agents (e.g., ethylenediaminetetraacetic acid, EDTA, or diethylenetetraaminepentaacetic acid, DTPA). The bleaching conditions are set as a temperature of about  $70^{\circ}\text{C}$  and an initial pH of 11-12, and an end pH of 8.5-9. For more detailed information of the bleaching process, see Lindholm (1999).

Bleaching of mechanical and chemimechanical pulps does not dissolve the coloured chromophores from the pulp; instead, they are reduced or oxidised into uncoloured products, i.e. leucochromophores. UV-irradiation or oxidation in the dark will then result in the uncoloured substances reverting to chromophores. In addition, bleaching can introduce new structures into the pulp which in turn may form other new chromophores. For example, Gellerstedt and Zhang (1993) showed that hydrogen peroxide bleaching of spruce ground wood pulp and CTMP leads to formation of stilbenes.

## **2.4 Light-induced discolouration**

When paper containing mechanical or chemimechanical pulp is subjected to sunlight or indoor illumination containing UV-radiation, it turns yellow. This yellowing, or rapid brightness reversion, is the major obstacle to mechanical or chemimechanical pulps being used in high-quality and long-life paper products. It is generally accepted that it is the lignin component that is responsible for the brightness reversion (Gratzl 1985; Heitner 1993b; Leary 1994; Davidson 1996; Forsskåhl 2000; Lanzalunga, Bietti 2000). The lignin forms compounds, chromophores, which absorb light in the blue-green region and turn the paper yellowish. Not all radiation is detrimental; wavelengths below approximately 385 nm cause yellowing, while wavelengths above approximately 385 nm have a bleaching effect. The transition from photo-yellowing to photo-bleaching of lignocellulosic materials around 385 nm has been shown by several researchers (Nolan et al. 1945; Leary 1967; Andtbacka et al. 1989; Mailly et al. 1996). The transition is, however, not fixed at a certain wavelength but depends on several factors, including the wood raw material, the pulping method used, and how the light-induced ageing is performed and evaluated (Heitner 1993a). A pulp bleached to higher brightness is more sensitive to irradiation and will suffer from light-induced discolouration to a greater extent than an unbleached pulp (Forsskåhl 2000). Despite this, the trend leans towards higher brightness and whiteness levels of SC, LWC, MWC and fine paper grades.

### **2.4.1 Influence of wood raw materials and pulping processes**

Brightness stability has been reported to differ depending on the wood species and the mechanical pulping processes employed. It has been claimed that the rate of chromophore formation is greater for bleached spruce TMP than for bleached spruce CTMP (Heitner, Min 1987). This was supported by the findings of Johnson (1989, 1991), who showed that CTMP are slightly more stable than TMP or groundwood pulps, and, moreover, that hardwood pulps are more stable than softwood pulp. Agnemo et al. (1991) contradict these findings stating that hydrogen peroxide bleached CTMP is somewhat more prone to yellowing than hydrogen peroxide bleached TMP. Other work has also shown that hardwood is

preferable to softwood as a raw material in this regard. Aspen pulps in particular seem to be more resistant to light-induced brightness reversion (Janson, Forsskåhl 1989; Paulsson, Ragauskas 1998b; Hu 2003). Aspen pulps have been suggested to not only have higher brightness stability compared to spruce, pine and birch pulps, but also to have higher initial brightness. Bond et al. (1999, 2001) showed that alkaline paper (lignin-containing and lignin-free) is more photo-stable than acid paper.

#### **2.4.2 Performing and evaluating light-induced ageing**

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. Because most researchers use their own ageing methods it is difficult to compare the results of these studies. Different exposure conditions (humidity, temperature etc.), light sources (light intensity, spectral distribution etc.), exposure times, the grammage of the exposed samples and the procedures chosen for quantifying the colour reversion greatly influence the experimental outcome. In the ambient ageing procedure, the irradiation source is often regular fluorescent light tubes, and the ageing generally takes place in an office environment. Even though the environment is realistic, it is hard to control the surrounding conditions, and the ageing procedure is time-consuming. On the other hand, accelerated light-induced ageing is very fast and the environmental factors can be controlled. The irradiation source often varies but subjects the samples to a very intense ageing. The wavelength distribution of the light source may resemble indoor irradiation, outdoor irradiation, both, or neither. Several investigations have shown that the spectral features of the light source used in photo-yellowing studies are of utmost importance (Paulsson, Ragauskas 1998b; Paulsson et al. 2002; McGarry et al. 2004). Obviously, in order to obtain realistic accelerated ageing conditions and thus relevant ageing results, one must use a light source that produces light resembling as closely as possible to that of the actual reversion situation.

Common properties to measure when evaluating light-induced discolouration are the brightness ( $R_{457}$ ) and light absorption coefficient ( $k$ ). Brightness ( $R_{457}$ ) is the reflectivity measured at an effective wavelength of 457 nm and is sensitive to changes that occur during bleaching (Pauler 2002). Brightness loss is dependent on the initial brightness (Johnson 1989; Forsskåhl 2000) and should not be used to compare samples with different brightness values. The light absorption coefficient ( $k$ ) is proportional to the amount of chromophoric substances in the pulps or papers and is usually measured at an effective wavelength of 457 nm or 557 nm. At 457 nm, the sensitivity for the chromophores responsible for the yellowish colour that is generated during the light-induced discolouration process is high, and is therefore the wavelength to prefer before 557 nm. However, it is hard to know

what a change in  $k$  value, means in terms of discolouration. Post colour number (PC number, or PCN) uses the Kubelka-Munk relationship to convert brightness loss to a parameter that is “linear” with respect to chromophore content, but only samples with similar light scattering coefficients ( $s$ ) can be compared. The CIELAB colour system provides more information regarding the actual colour change of the sample. It consists of three parameters where the  $L^*$  coordinate represents the lightness (or greyscale axis), the  $a^*$  coordinate the red (positive)/green (negative) axis, and the  $b^*$  coordinate the yellow (positive)/blue (negative) axis (Pauler 2002). Together, the  $L^*$ ,  $a^*$  and  $b^*$  values give a very detailed information about discolouration.

### **2.4.3 Light-induced ageing phases**

Generally, light-induced discolouration is reported to be characterised by a rapid initial phase during which most of the discolouration takes place, followed by a slower, less detrimental phase (Lewis et al. 1945; Francis et al. 1991; Ek 1992). However, the radiation source is known to influence both phases. Light-induced ageing using low-intensity UV-VIS fluorescent lamps generates a less pronounced initial phase (Paulsson et al. 1998b).

Luo et al. (1988, 1989) subjected a bleached groundwood pulp to five hours of accelerated light-induced ageing and observed the typical rapid initial phase for the  $L^*$  and  $b^*$  values, followed by a slower phase. According to Andrady et al. (1991), illumination with wavelengths below 400 nm cause yellowing (higher  $b^*$  value, while the  $a^*$  value remain unchanged) and wavelengths above 400 nm have a bleaching effect (no change in  $b^*$  value and a small change towards greenish in  $a^*$  value). This finding is supported by Paulsson and Ragauskas (1998b), who used three sets of lamps with different spectral distributions to study accelerated ageing of hydrogen peroxide bleached aspen and spruce CTMPs.

### **2.4.4 Light-induced ageing-mechanism**

#### **2.4.4.1 Historical background**

It was noticed as early as the late 19th century, that paper made from wood pulp deteriorated after a few years, while paper made from cotton remained in perfect condition (Johnson 1891). There was also some discussion over whether or not paper made from wood-cellulose should be used for paper that was intended to remain sound for long periods, since unbleached cellulose and groundwood were known to deteriorate rapidly (Herzberg 1895). Cross (1897) and Evans (1898) stated early on that oxygen was one cause of the discolouration of groundwood pulps. A few years later, Klemm (1901, 1902) found that wood-free papers were also susceptible to discolouration when sized with rosin. This was suggested to be attributed to the light-sensitive soaps which were contained in the paper,

consisting of iron in combination with organic acids of the rosin. Qualitative tests of the yellow discolouration confirmed that the product was an iron-rosin soap.

Schoeller (1912) compared the discolouration of a number of papers, and concluded that wood-containing papers reverted most rapidly whereas paper containing chemical pulp was more stable. Paper produced entirely from rag pulp was the most resistant material, showing only a slight discolouration. This result was verified by Zschokke (1913), and it was also reported that apart from mechanical pulp, rosin size was the sole cause of discolouration. The change in colour was due to heat and light, while atmospheric oxidation was considered to have very little effect on the action.

In 1920, Aribert and Bouvier established that the yellowing of groundwood paper was caused by the oxidation of fats, waxes, resins and lignin. Moreover, Sindall (1920) suggested that the discolouration process was caused by a slow oxidation of non-cellulosic constituents in the pulp. The transformation of cell membranes into humus has also been suggested as a reason for darkening of groundwood pulp under atmospheric conditions (Hirschkind 1932). Later on (Bakker 1937), it was proposed that humic acid was formed through the oxidation of lignin when groundwood paper was subjected to sunlight or ultraviolet (UV) radiation.

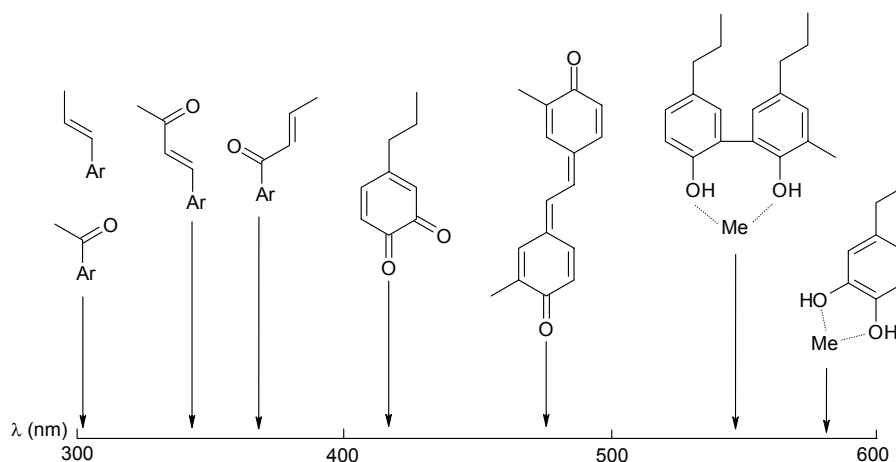
It was not until the forties that the chemical changes of pulp and paper during brightness reversion were studied. Forman (1940) found that irradiation of lignin decreased its methoxyl content. Impregnation of groundwood sheets with vanillin (one of the lignin degradation products) caused extensive brightness reversion. Demethoxylation of lignin was also reported by Lewis and Fronmuller (1945) when exposing groundwood sheets to ultraviolet radiation; other effects observed were shortening of the cellulose chains and an increase in the uronic acid content.

Launer and Wilson (1943) showed that radiation in the near ultraviolet region caused bleaching of cellulose, while radiation in the far ultraviolet region caused yellowing of the same. In 1945, Nolan et al. showed that radiation in the 385-400 nm range bleached groundwood, pulp while irradiation below ~385 nm caused yellowing (cf. discussion under section 2.4).

#### **2.4.4.2 Radical formation**

Lin and Kringstad (1970) found that when milled wood lignin and lignin model compounds were exposed to ultraviolet radiation, biphenyl,  $\alpha$ -carbonyl and ring-conjugated double bond structures formed coloured compounds. Of the structures capable of absorbing UV radiation, the  $\alpha$ -carbonyl group has been considered to be the most important photo-catalyst (Forsskåhl 1984). *Ortho*- and *para*-quinones are considered to be the chromophores that initially are formed during light-induced discolouration (cf. section 2.4.4.3). Another type of chromophores that could be

formed e.g. in the mechanical pulping process are metal complexes with catechols or phenolic biphenyl units. According to Gratzl (1985), the most important part of the sunlight spectrum in terms of yellowing and darkening is that between 300 and 550 nm, since the majority of lignin leucochromophores and chromophores absorb energy in this wavelength interval (Figure 1).

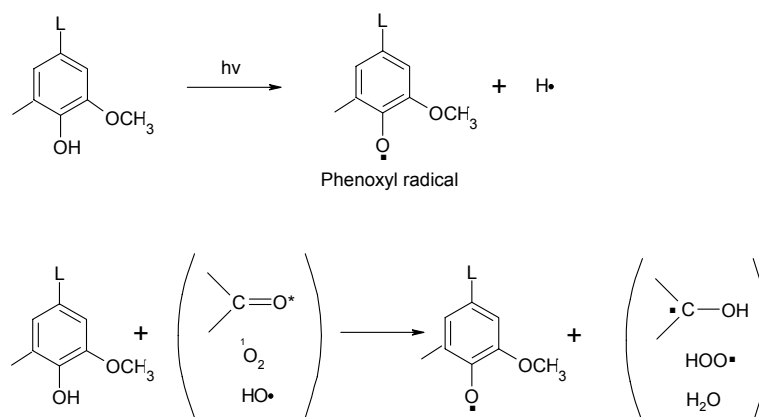


**Figure 1.** Possible leucochromophores and chromophores in lignin and their approximate absorbance maxima (adapted from Gratzl 1985).

Monomeric substituted *ortho*-quinones in lignin-rich pulps show a sharp absorption maxima peak at 423-444 nm, monomeric substituted *para*-quinones exhibit somewhat lower absorption maxima; between 408-417 nm, dimeric quinone structures usually give a broad peak at higher wavelengths (Zhang, Gellerstedt 1994b). The absorption maxima of different types of chromophores are further discussed in section 2.4.4.3.

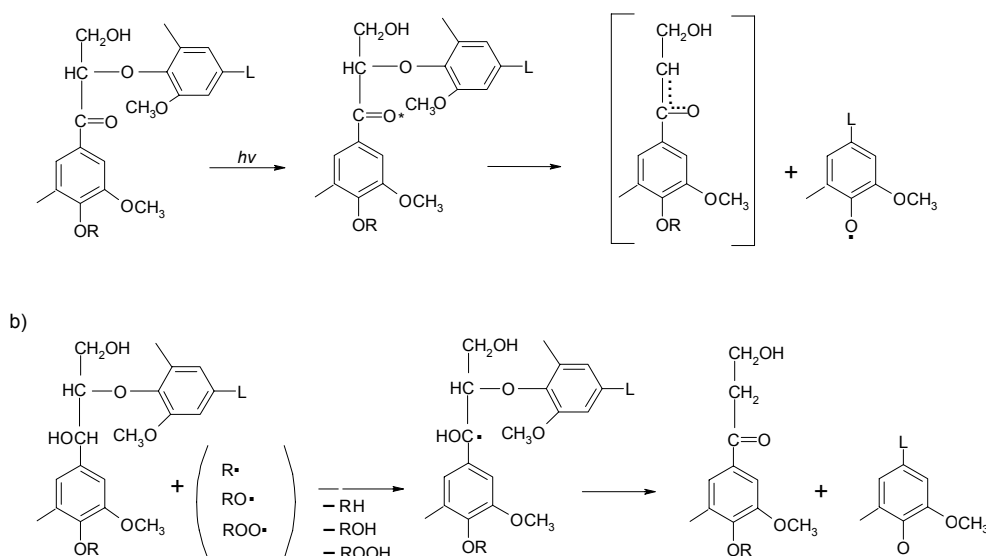
Most of the proposed mechanisms behind light-induced discolouration involve phenoxyl radicals. The phenoxyl radicals can be formed via oxidation of free phenolic hydroxyl groups (Figure 2). Direct photolysis of phenolic compounds has been suggested by several researchers (Kringstad, Lin 1970; Fornier de Violet et al. 1989) as one mechanism. Another is the abstraction of phenolic hydrogen atoms by excited structures (Leary 1968; Kringstad, Lin 1970). It has also been proposed that oxygen molecules can act as energy-transferring agents (Brunow, Sivonen 1975) and give rise to a singlet (excited) oxygen molecule ( $^1\text{O}_2$ ), which in turn can react with a phenolic group (cf. Figure 2). Hydroxyl and alkoxyl radicals can be formed by photolytic cleavage of peroxide structures, and it has been suggested that these radicals are involved in a hydrogen atom abstraction mechanism leading to phenoxyl radicals (Gratzl 1985). Agnemo et al. (1991) also have identified hydroxyl

radicals in TMP and CTMP sheets during irradiation, and suggest that these radicals are involved in the discolouration mechanism.



**Figure 2.** Formation of phenoxy radicals from phenolic hydroxyl groups. L is a polymeric part of the lignin polymer.

Gierer and Lin (1972) observed a fragmentation of a 2-aryloxy-1-arylpropanone structure upon near UV-irradiation. They suggested that cleavage of the  $\beta$ -aryl ether bonds takes place directly from the excited state leading to phenoxy and phenacyl radicals (reaction pathway a) in Figure 3). The cleavage of 2-aryloxy-1-arylpropanone structures was later confirmed for both non-phenolic and phenolic lignin model compounds (Castellan et al. 1988, 1989; Scaiano et al. 1991).  $\alpha$ -Carbonylic structures might be formed from oxidation of benzylic groups by photo-excited carbonyls (Scaiano 1973; Schmidt et al. 1990; Francis et al. 1991). Schmidt and Heitner (1993, 1995) have proposed a mechanism that involves cleavage of arylglycerol- $\beta$ -aryl ethers and formation of phenoxy radicals and aromatic ketones (pathway b) in Figure 3). The majority of the inter-unit linkages in lignin are of this type and it also results in the formation of new phenolic groups and new  $\alpha$ -carbonyls. It was also stated that as much as 70% of the colour formed during radiation might be attributed to this “ketyl radical pathway”.

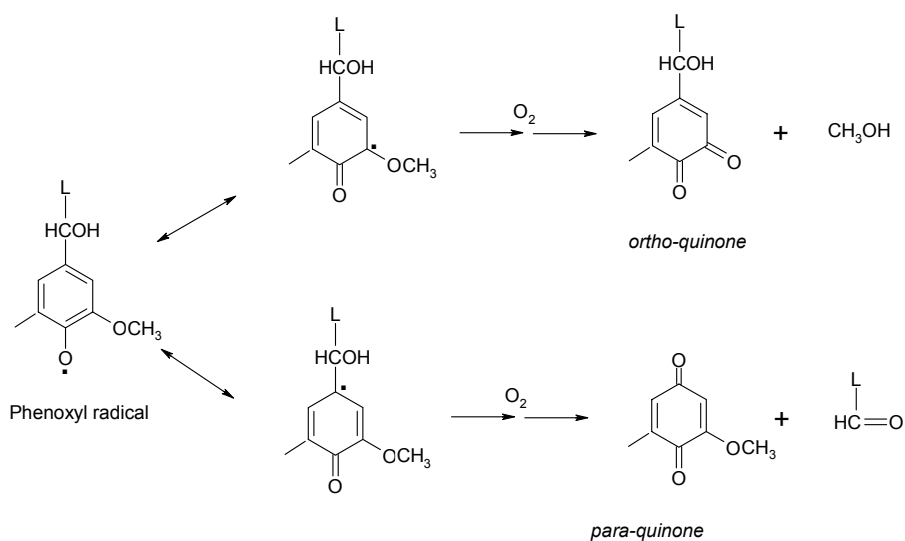


**Figure 3.** Formation of phenoxyl radicals by cleavage of β-aryl ether structures. L is a polymeric part of the lignin polymer. R = H or C.

#### 2.4.4.3 Chromophore formation

There have been a number of investigations focusing on the type of chromophores that are initially formed during light-induced discolouration. Leary (1968) proposed that the chromophores formed during light-induced yellowing were of the quinone, cyclohexadienone and/or quinone methide types. Lin and Kringstad (1971) suggested, based on lignin model compound studies, that both *ortho*- and *para*-quinones can be formed (Figure 4), although the latter to a lesser extent (cf. Lebo et al. 1990). *Ortho*-quinones are produced by demethylation that generates methanol as one end-product, and this agrees with the observed decrease in methoxyl content upon irradiation of lignin, (see section 2.4.4.1, Leary 1968). Argyropoulos and coworkers (1995) found that during the early stages of photo-degradation there is a rapid formation of *ortho*-quinones that subsequently react further to form more complex chromophores of non-quinoid nature.

*Para*-quinone structures were suggested to contribute to the formation of colour during light-induced discolouring (Gellerstedt, Pettersson 1977; Forsskåhl et al. 1991; Hirashima, Sumimoto 1994). This implication was supported by Agarwal (1999, 2005), who proposed a hydroquinone/*para*-quinone redox couple as a leucochromophoric/chromophoric system responsible for the discolouration. The formation of *para*-quinones by cleavage of the side chain is shown in Figure 4.



**Figure 4.** Formation of quinoid chromophores from phenoxy radicals. L is a polymeric part of the lignin polymer.

Hydroxystilbenes have also been proposed as the leucochromophores that are largely responsible for the initial photo-induced discolouration of bleached high-yield pulps (Gellerstedt, Zhang 1993). Furthermore, Zhang and Gellerstedt (1994a) synthesized and irradiated two monohydroxystilbene model compounds with outdoor sunlight to study the mechanism of photo-yellowing in the solid state. A stilbene *ortho*-quinone was found to be the structure responsible for the formation of colour, although its yield was estimated to be the lowest among the products identified. The stilbene *ortho*-quinone showed a reddish colour in solution with  $\lambda_{max}$  at 424 nm. The key step in the reaction sequence, leading to the formation of a stilbene phenoxy radical, is initiated by a sequential electron transfer-proton transfer process.

Diguaiacyl stilbenes mostly produced from diarylpropane structures during hydrogen peroxide bleaching are the predominant leucochromophoric structure present in hydrogen bleached pulps and these seem to be responsible for a major portion of the fast photo-yellowing of these pulps (Gellerstedt, Zhang 1992). According to Castellan et al. (1990) diguaiacyl stilbenes and phenylcoumarones bearing free phenolic hydroxyl groups are among the most sensitive leucochromophoric structures.

When treating GWP, TMP and CTMP with hydrogen peroxide, chromophores that absorb light at wavelengths in the range 360 to 460 nm are oxidised (Holah, Heitner 1991). Coniferaldehyde end groups have a strong absorption of UV-radiation, at wavelengths round 350 nm. Coniferaldehyde structures, the major leucochromophore originally present in spruce wood lignin, are reduced during

the CTMP process and eliminated after bleaching with hydrogen peroxide. Gellerstedt and Zhang (1993) claim that coniferyl alcohol end groups are rather stable during high-yield pulping processes and that the GWP and CTMP pulping processes may possibly result in a slightly reduced content of such end groups but hydrogen peroxide bleaching seems not to lead to any further reduction.

There could be many reasons for the discrepancy in reported results. A high-yield pulp contains a variety of organic compounds, and the complexity of the lignocellulosic system makes it likely that different types of chromophores are formed during light-induced ageing. The disagreements could also be due to the fact that the studies used different equipments and experimental setups. Most of the investigations employed accelerated ageing procedures, which sometimes give other results than ageing under conditions closer to the practical everyday situation (Paulsson, Parkås 2001; McGarry et al. 2004; Paper I, II). Moreover, to determine the absorption maxima for different types of chromophores that are suggested to be formed during light-induced discolouration is not a simple and straightforward procedure. Model compounds representing differently substituted *ortho*- and *para*-quinones were studied by UV-VIS spectroscopy by recording the spectra of the compounds in solution or when applied onto filter paper or bleached high-yield pulps. The absorption bands of the quinone structures were intensively red shifted when impregnated onto lignin-rich pulp. For most quinones the red shift was around 20 nm on filter paper, and on high yield pulps from 32 to 148 nm. Zhang and Gellerstedt (1994b) suggested that the formation of a charge-transfer complex between phenol and quinone might account for the large red shift effects.

## **2.5 Inhibition of light-induced discolouration**

The brightness reversion of groundwood papers has been known since the late 19th century (cf. section 2.4.4.1). Over the years, there have been a number of attempts to inhibit or slow down the light-induced yellowing of lignocellulosic materials. A summary of the proposed main pathways is given below.

### **2.5.1 Chemical modifications**

One approach to preventing photo-yellowing involves chemical modification of the reactive structures in lignin to suppress the formation of chromophores. Reduction of the  $\alpha$ -carbonyl groups in lignin by sodium borohydride ( $\text{NaBH}_4$ ) has been reported to considerably improve the photo-stability of spruce milled wood lignin (Lin, Kringstad 1970). However, when the same reduction was tested on spruce GWP, the effect was minor (Leary 1968; Ek et al. 1990). It was later found that neither TMP nor CTMP were significantly stabilised by  $\text{NaBH}_4$ -reduction (Fornier de Violet et al. 1989; Francis et al. 1991; Schmidt, Heitner 1991; Paulsson et al. 1995).

Another approach involves chemically modifying the lignin by etherifying or esterifying hydroxyl groups. Methylation and acetylation are the most frequently used treatments, although propionylation has also been used. Methylation of groundwood-based newsprint with dimethyl sulphate was found to increase its photo-stability and brightness (Leary 1968). However, other research has shown that although methylation with dimethyl sulphate and alkali has a positive effect on photo-stabilisation, it has a negative effect on the initial brightness (Andrews, Des Rosiers 1966). Paulson and Simonson (2002) reported that acetylating paper made from spruce TMP not only extensively retarded photo-yellowing but also produced brighter unbleached pulp. Pu et al. (2003) showed that the inhibiting effects of acetylation of lignin isolated from bleached spruce CTMP most likely is attributed to the removal of quinoidal structures and the acetylation of phenoxy and aliphatic hydroxyl groups. The fact that acetylation both brighten and photo-stabilise groundwood pulp have been noted by other researchers (Manchester et al. 1960; Lorås 1968; Ek et al. 1992). Propionylation of a bleached spruce CTMP has also been reported to stabilise the pulp against photo-yellowing (Paulsson, Parkås 2000).

### **2.5.2 Additives to the pulp furnish**

Another way to improve the light stability is to shield the paper from damaging ultraviolet radiation by using UV-absorbers. Kringstad (1969) showed a decrease in brightness reversion for a hydrogen peroxide bleached groundwood pulp treated with two benzophenone derivates (2-2'-dihydroxy-4-methoxy-benzophenone and 2-2',4-4'-tetrahydroxybenzophenone). The same results were obtained with 2,4-dihydroxybenzophenone and spruce groundwood pulps (Gellerstedt et al. 1983; Fournier de Violet et al. 1990). Others have also reported stabilising effects when derivates of hydroxymethoxybenzophenone and dihydroxybenzophenone were added to paper based on high-yield pulp (Argyropoulos et al. 2000; Peng, Argyropoulos 2000; Weir, Miller 2000).

Many researchers have also used a fluorescent whitening agent (FWA) to inhibit brightness reversion (Bourgoing, Robert 1997; Bourgoing et al. 2001; Ragauskas et al. 2001). The usage of FWA is further discussed in section 2.5.3.4.

Given that radicals play an important role in the brightness reversion process, antioxidants, which are known to be free radical scavengers, have the potential to be used as yellowing inhibitors. Sodium citrate and sodium ascorbate was reported to reduce the photo-yellowing of bleached groundwood pulp (Kringstad 1969), as can ascorbic acid, when added to a hydrogen peroxide bleached TMP (Agnemo et al. 1991, Agnemo 1992). Unfortunately, however, the antioxidants are consumed with time, and the inhibitory effect is only temporary (Janson, Forsskåhl 1989; Schmidt, Heitner 1991). In addition, ascorbic acid increases thermal yellowing (Ragauskas 1994; Schmidt, Heitner 1997).

Sulphur containing compounds such as thiols and thioethers also have a stabilising effect on high-yield pulp (Cole, Sarkanen 1997). Thiols have the further advantage that they bleach the pulp (Pan et al. 1996; Cole et al. 2000; Spender et al. 2000). Despite all the findings reported above, no satisfactory, (i.e., cost-efficient, technically feasible, and non-toxic) method of slowing down the yellowing rate has so far been discovered.

### **2.5.3 Coating**

Coating of paper has the potential to retard light-induced discolouration by preventing the damaging radiation from reaching the paper. A typical coating formulation consists of pigment, binder, thickener and additives, all of which can affect the photo-stability of the base paper.

#### **2.5.3.1 Coat weight**

The amount of coating will of course affect the ability of the light to pass through the coating layer. The higher the coat weight (i.e. thicker coating layer), the harder it is for the light to reach the surface of the paper (Ghosh 2002). For example, at a coat weight of 4 g/m<sup>2</sup>, the light-induced discolouration, measured as  $\Delta K_{457}$ , was decreased with 20% compared to an uncoated paper. Increasing the coat weight to 7 g/m<sup>2</sup>, resulted in a 40% decrease in light-induced discolouration (Johnson 1991).

#### **2.5.3.2 Pigments**

The type of pigments in the coating colour can vary from relatively low-cost natural mineral pigments (e.g. kaolin clay, calcium carbonate, talc) to synthetic inorganic or organic products (e.g., plastic and silica type products). Fossum et al. (1976) showed that a 10–15 g/m<sup>2</sup> coating layer, containing clay, on each side of a base paper (spruce; 70% TMP, 30% sulphite) was somewhat more effective in retarding accelerated (xenon lamp) light-induced yellowing than a coating layer with calcium carbonate pigments. This was supported by Luo and Götsching (1991) who reported that kaolin was somewhat more effective than a brighter calcium carbonate pigment in retarding the photo-yellowing of a base paper intended for light weight coated paper grades. They also found that combining kaolin and calcium carbonate pigments improved the performance to some extent. On the other hand, Krogerus and Forsskåhl (1995) found that calcium carbonate was superior to other pigments in inhibiting light-induced ageing. Addition of TiO<sub>2</sub> to the coating formulation further improves the retardation of paper degradation (cf. Johnson 1991; Yuan et al. 2003 and discussion below in section 2.5.3.4).

The particle size distribution of the pigment is also known to have an effect on the light-scattering ability of a coating layer (Lindblad et al. 1989; Bown 1997). A

steep particle size distribution gives poor packing, which creates void space in the dried structures that may enhance light scattering. If maximum light scattering is desired in a certain wavelength region (e.g., the UV-region), the pore diameter should be such that the ratio of pore diameter to wavelength is approximately 0.5 and all the pores should preferably be of the same size (Lindblad et al. 1989). A monodisperse pigment particle system of this type could offer high UV-scattering ability that might considerably improve photo-stability. It is thus important to examine the effect of particle size and the particle size distribution of commercial coating pigments on the UV-screening properties of coating layers.

#### **2.5.3.3 Binders**

Binders have multiple functions; binding the pigment particles together, binding the pigment particles to the base paper, and partially filling the voids between the pigment particles. Moreover, they affect the viscosity and water retention of the coating colour. Binders and thickeners both also affect the brightness stability of the coating colour; for example, polyester-polynitrile is more photo-stable than butadiene-styrene (Reinhardt, Arneberg 1988; Luo, Götsching 1991).

#### **2.5.3.4 UV-absorbing additives**

Fluorescent whitening agents (FWA) absorb light in the UV-region and emit light in the blue wavelength region, making paper appear whiter. The use of FWA to inhibit brightness reversion of paper made from mechanical and chemimechanical pulp has been suggested by several researchers. Ragauskas et al. (2001) reported that hardwood CTMP treated with a diaminostilbene-based FWA retarded brightness reversion by 25% compared to untreated paper. Furthermore, up to an 80% reduction in chromophore formation after 5 hours of UV-irradiation has been shown to result when FWA was sprayed onto unbleached TMP (Bourgoing, Robert 1997; Bourgoing et al. 2001).

Carriers for FWA, such as starch, polyethylene glycol (PEG), polyvinyl alcohol (PVOH), carboxymethylcellulose (CMC) and polyvinylpyrrolidone (PVP) can also influence the photo-stability of lignin-containing pulps (Rohringer, Fletcher 1996; Paulsson, Ragauskas 1998a). PEG with different molecular weights and different end groups has been used to prevent light-induced discolouration, but relatively large amounts are needed (Minemura 1978; Janson, Forsskåhl 1989; Ragauskas et al. 2001). As well as inhibiting photo-discolouration, PVP has also been found to increase the initial brightness (Hortling et al. 1993; Rättö et al. 1993). Polytetrahydrofuran (PTHF) is another polymer that has been used to reduce brightness reversion (Janson, Forsskåhl 1996). Another way of inhibiting light-induced discolouration is to use UV-absorbers (UVA) in the pulp, on the paper surface or in the coating colour to block out damageing UV-radiation. Derivates of

benzophenone has been found to have a positive effect on brightness reversion (Kringstad 1969; Gellerstedt et al. 1983; Fornier de Violet et al. 1990; Paulsson, Ragauskas 1998b; Argyropoulos et al. 2000; Peng, Argyropoulos 2000; Weir, Miller 2000). Applying a combination of UVA (a hydroxyphenylbenzotriazole), radical scavenger (RS, 4-hydroxy-2,2,6,6-tetramethyl-*N*-hydroxypiperidine) and TiO<sub>2</sub> to alkaline peroxide mechanical pulp (55% spruce and 45% aspen) resulted in higher initial brightness and better brightness stability without affecting the rheology of the coating colour (Yuan et al. 2004). The same UVA and RS was used in the work by El-Sadi et al. (2002), which reported that the yellowing inhibition is most sensitive to total inhibitor charge, and strongly depends on the RS/UVA ratio.

Titanium dioxide (TiO<sub>2</sub>) is the most efficient opacity-increasing pigment of the pigments commonly used, due to its high light scattering ability, which in turn is a result of its high refractive index. The photo-stabilisation effect (measured as  $\Delta k_{457}$ ) improved by 40% when substituting 5 parts of a clay with TiO<sub>2</sub> (Johnson 1991). Substituting 10 parts of the clay resulted in a 50% improvement, and a 60% enhancement was achieved when 20 parts of the clay were substituted with TiO<sub>2</sub>. The base paper consisted of aspen CTMP and was coated using laboratory lick-coating equipment. The stabilisation effects were evaluated using two Sylvania 275 W RSM sunlamps. Yuan et al. (2003) reported that after 90 days of exposure to office light (eight 8 W cool-white fluorescent lamps), a coated (calcium carbonate/kaolin, 9 g/m<sup>2</sup>) paper produced from alkaline peroxide mechanical pulp lost 2.8 ISO brightness points when 0.67% TiO<sub>2</sub> and 0.18% RS (same RS as mentioned above) were added to the coating colour, compared to 7.0 points for the coated control. Recently, it was reported (Yuan et al. 2006) that a coated (calcium carbonate, 80 parts/delaminated clay, 20 parts, 20 g/m<sup>2</sup>) sheet from a kraft pulp with a 15% substitution of bleached birch CTMP gave the same brightness stability as a 100% kraft sheet coated at 4 g/m<sup>2</sup>. The evaluation involved both accelerated (fluorescent lamps) and natural long-term light-induced ageing.

### 3. EXPERIMENTAL

*This chapter provides a brief presentation of the materials and methods; the final section describes the new method that was developed for studying the reflectance/transmittance properties of thin coating layers in relation to their effect of light-induced discolouration. Details of the individual experiments conducted can be found in the appended Papers I - V.*

#### 3.1 Materials

Table 2 presents the abbreviations of the examined pulps. The characteristics of the mechanical and chemimechanical pulps and kaolin and calcium carbonate pigments used are shown in Tables 3-5.

**Table 2.** 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 Kraft pulp

**Table 3.** Pulp characteristics (brightness, bleaching chemicals, lignin and extractive contents) before ageing of the examined softwood and hardwood high-yield pulps.

	Type of pulp <sup>1)</sup>	Initial brightness (% ISO)	Bleaching chemicals	Total lignin content (%) <sup>2)</sup>	Acid-soluble lignin (%)	Extractives (%) <sup>5)</sup>
<b>Spruce</b> ( <i>Picea abies</i> )	HTCTMP	58.4	—	26.8	0.2	0.2
	TMP	61.2	—	27.9	0.1	0.2
	BTMP	64.2	Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub>	27.1	0.1	0.1
	BGWP	64.6	Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub>	28.0	0.1	0.2
	BGWP <sup>3)</sup>	73.4	H <sub>2</sub> O <sub>2</sub> + Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub>	28.4	0.2	0.1
	BHTCTMP	74.0	H <sub>2</sub> O <sub>2</sub>	25.3	0.3	0.1
	BGWP	74.5	H <sub>2</sub> O <sub>2</sub>	28.1	0.2	0.2
	BTMP	74.7	H <sub>2</sub> O <sub>2</sub>	27.8	0.2	0.1
	BCTMP	75.8	H <sub>2</sub> O <sub>2</sub>	25.7	0.3	0.0
<b>Birch</b> ( <i>Betula verrucosa</i> )	CTMP	53.7	—	23.5	4.5	0.2
	CTMP	62.4	—	21.7	4.6	0.2
	HTCTMP	63.0	Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub>	23.0	4.9	0.3
	HTCTMP	63.4	—	23.3	5.1	0.3
	BCTMP	79.3	H <sub>2</sub> O <sub>2</sub>	21.6	4.6	0.1
	APMP <sup>4)</sup>	80.4	H <sub>2</sub> O <sub>2</sub>	21.1	6.4	0.1
<b>Aspen</b> ( <i>Populus tremula</i> )	BCTMP	65.7	—	24.4	2.6	0.3
	BCTMP	78.5	H <sub>2</sub> O <sub>2</sub>	22.2	3.3	0.1
	BGWP	81.4	H <sub>2</sub> O <sub>2</sub>	21.3	3.0	0.2
	APMP <sup>4)</sup>	83.8	H <sub>2</sub> O <sub>2</sub>	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.

5). CH<sub>2</sub>Cl<sub>2</sub> (dichloromethane, DCM).

**Table 4.** Data for the kaolin pigments investigated in this thesis, as obtained from Imerys. The notation (A) implies that the pigments are from the same source.

Pigment	Bleached / Unbleached B / U	<2µm	<1µm	Wt% <0.5µm	<0.25µm	<0.10µm	D50, µm <sup>2)</sup>	Surface area (m <sup>2</sup> /g)	Brightness (% ISO)
<b>Kaolin clays</b>									
Astra-Plus	U	93	78	52	23	4	0.49	13	86.9
Astra-Plus (A)	U	95	81	52	18	n.a. <sup>3)</sup>	0.45	11.6	86.2
Astra-Plus (A)	B	98	84	52	17	n.a. <sup>3)</sup>	0.45	12.2	88.2
Alphatex. <sup>1)</sup>	U	90	80	40	6	n.a. <sup>3)</sup>	0.60	13	91.6
Supragloss 95	U	91	75	55	28	15	0.46	16	86.8
Astra-Sheen	U	99	97	90	61	28	0.31	27	88.7

1). Alphatex is a calcined clay and is aggregated. The particle size distribution measured by Sedigraph assumes that the particles have a density of 2.65 g/cm<sup>3</sup>. However, the aggregates will have a pore structure which will be filled with water, lowering the effective particle density to somewhere between 1.00 and 2.65 g/cm<sup>3</sup>. Hence the real aggregate size distribution will be coarser than reported here.

2). Median particle size.

3). Not available.

**Table 5.** Data for the ground (GCC) and precipitated (PCC) calcium carbonate pigments investigated in this thesis, as obtained from Imerys. The notation (A) implies that the pigments are from the same source.

Pigment	Bleached / Unbleached B / U	<2µm	<1µm	Wt% <0.5µm	<0.25µm	<0.10µm	D50, µm <sup>1)</sup>	Surface area (m <sup>2</sup> /g)	Brightness (% ISO)
<b>GCC</b>									
Carbital 60	U	60	40	25	13	n.a. <sup>2)</sup>	1.5	n.a. <sup>2)</sup>	95.0
Carbital 60 (A)	U	63	40	22	11	5	1.5	7.6	95.3
Carbital 90 (A)	U	91	63	37	20	10	0.72	12.0	94.7
Carbital 90 (A)	B	88	60	36	19	9	0.77	11.8	95.1
Carbital 95	U	95	80	50	30	15	0.45	15.0	94.5
Carbopaque 90	U	88	60	26	12	n.a. <sup>2)</sup>	0.80	11	95.4
<b>PCC</b>									
Opti-Cal Print 400	U	97	95	75	16	n.a. <sup>2)</sup>	0.40	9.2	96.0
Opti-Cal Print 600	U	97	90	36	2	n.a. <sup>2)</sup>	0.57	7.4	96.6

1). Median particle size.

2). Not available.

## 3.2 Light-induced ageing methods

An ageing procedure has to be adopted when evaluating light-induced brightness reversion. This procedure can involve accelerated or ambient ageing (cf. section 2.4.2). The methods used in the current thesis are described in the following paragraphs.

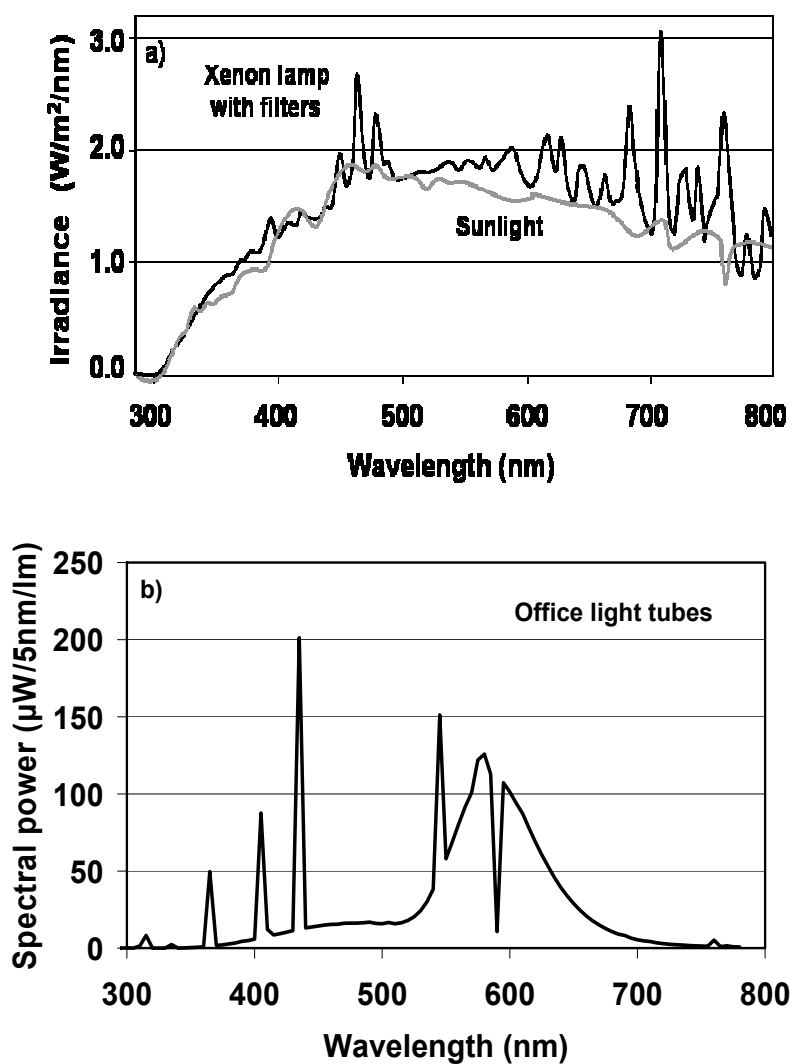
### 3.2.1 Accelerated light-induced ageing

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 at wavelengths below 310 nm. The spectral characteristics of the transmitted light are similar to those of average indoor daylight, that is, of sunlight through window glass (Paulsson, Ragauskas 1998b); these characteristics are given in Figure 5a. The temperature was kept close to room temperature by means of a cooling fan. To compensate for any main voltage fluctuations and lamp ageing, the irradiance was controlled with an optical sensor. The irradiance in the UV-A region was approximately 40 W/m<sup>2</sup>.

### 3.2.2 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 for 10 hours per day to simulate an office environment. No indirect sunlight reached the paper samples. The spectral characteristics of the light source are given in Figure 5b.



**Figures 5a-b.** The spectral characteristics of the light sources used for (a) the accelerated and (b) the ambient light-induced ageing procedures. The spectral energy distribution of sunlight is given in Figure 1a for the purposes of comparison.

### 3.3 Coating procedure (Paper III-V)

In order to study the transmittance and reflectance of thin coating layers in a reproducible way, quartz glass plates were coated in a laboratory coater using a glass rod to spread the coating colour. The speed of the rod was varied to obtain various coat weights. The coating layer was dried at room temperature before UV-VIS spectroscopic analysis.

The standard coating formulation consisted of a pigment (100 parts), styrene-butadiene (SB) latex (8 parts) and carboxymethylcellulose (CMC) (0.5 parts). When investigating different binders (cf. section 4.3.2), the styrene butadiene latex was exchanged for five or ten parts of polyvinylpyrrolidone (PVP) or polyvinyl alcohol (PVOH). The pH of the coating colour was adjusted to 8.5 with 5M NaOH. To determine the coat weight, coating colour on a known area (the same area used to record the UV-VIS spectra) was scraped off and weighed after drying at 105°C. Coat weights are given in g/m<sup>2</sup>.

### 3.4 UV-VIS diffuse reflectance spectroscopy (Paper III-V)

UV-VIS spectra were recorded on a UV-Visible spectrophotometer (Varian Cary 100 Bio). Spectral data were obtained by changing the wavelength of the illumination from 200–700 nm in steps of 1 nm. The scan rate was 600 nm/min. The resulting spectra for each sampling point are mean values from at least 3 measurements.

As for the majority of optical instruments, the measured values are not the total amount of light reflected or transmitted in every direction, but a well defined fraction of it. To account for the specific conditions set by the instrument and the procedures, the optical values are referred to as transmittance factors,  $T_F$ , or reflectance factors,  $R_F$ . The transmittance factors were measured in two ways as described below.

1. 0°/0° geometry. A straight forward approach where the sample was placed in the cuvette holder of the spectrometer, illuminated with a single light beam at 0° to the normal of its surface, in case of coated samples with the bare glass surface facing the beam. The detector was situated on the other side of the sample, directly opposite to the incoming beam, thus giving a direct measurement of the transmitted light in that direction. Zero/baseline correction was used to calibrate the instrument: a measurement in air only, with no sample in the beam, gave a 100% transmittance scan, the beam was then completely blocked to collect a 0% transmittance baseline. When performing the measurements using the 0°/0° geometry, the transmittance factor is referred to as  $T_{dir}$ .
2. 0°/d geometry. The spectrophotometer was equipped with a 70-mm diameter integrating sphere coated with Spectralon® (DRA-CA-301). The light came

into the sphere through an opening on the side, at the “equator”. The quartz glass sample was placed over this opening, so that the illuminating light passed through the sample before entering the sphere. The sample was illuminated at  $0^\circ$  to the normal, and the bare glass surface of the coated samples was facing the beam. The detector was placed at the bottom of the sphere (corresponding to the “south pole”) thus collecting most of the light which was transmitted through the sample in all directions. Another opening in the sphere was covered with a Spectralon® diffuse white standard (Labsphere). When performing the measurements using the  $0^\circ/0^\circ$  geometry, the transmittance factor is referred to as  $T_{sphere}$ .

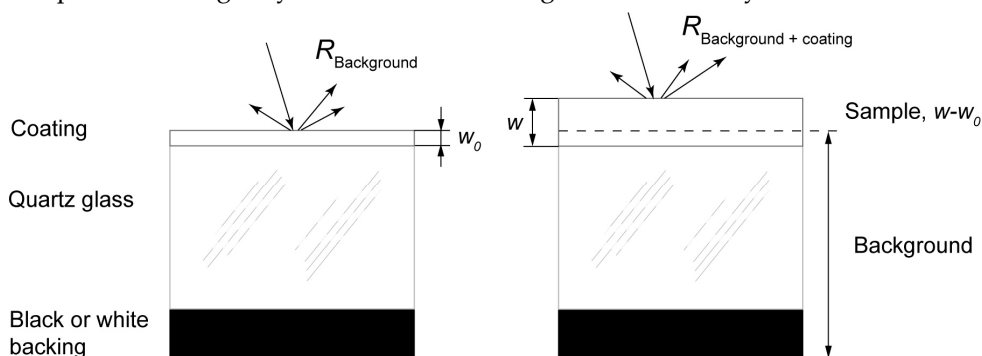
Diffuse reflectance factors were measured in a similar way using ( $0^\circ/d$ ) geometry. The sample was placed over an opening in the sphere directly opposite to the opening for the incoming illumination, which means that the sample was illuminated at  $0^\circ$  to the normal of its surface. In this case the coating layer was facing the beam and a black or white background was used since all samples are transparent to some degree. A pile of Tyvek® (DuPont) was used as white background and black velvet was used as black background with the front side facing the sample. Diffuse detection took place as above. Baseline correction was used for calibration; a 100% reflectance baseline was collected by measuring a Spectralon® diffuse white standard (Labsphere).

The mean value of the transmittance factors,  $T_F$ , between 300–385 nm was chosen to represent the ability of the coatings to block radiation in the UV-region of the spectrum (cf. section 2.4). The transmittance of the uncoated quartz glass plates determined in this way was in the range of 90–93%.

To evaluate the coatings, the transmittance properties were determined for a plate of quartz glass, a coating layer was then applied to this quartz glass and the same measurement procedure followed. The transmittance factor of the coating layer as such,  $T_C$ , was calculated by dividing the transmittance factor (300–385 nm) of the coated quartz glass plate,  $T_{GC}$ , by the transmittance factor (300–385 nm) of the bare glass plate,  $T_G$ . This is motivated by the fact that  $T_{GC}$  is defined as the ratio of the transmitted intensity  $I_{GC}$  and the illumination  $I_0$ , (multiplied by 100 to be expressed in %) and in the same way for the quartz glass,  $T_G = I_G/I_0$ . Considering that in the case of a coating layer on the backside of the glass, the intensity reaching the coating layer is that transmitted through the glass,  $I_G$ , and that the intensity transmitted through the coating is  $I_{GC}$ , the transmittance of the coating layer,  $T_C$ , becomes:  $I_{GC}/I_G = T_{GC}I_0/T_GI_0 = T_{GC}/T_G$ .

### 3.4.1 Determination of $s$ and $k$ values for the coatings

The calculation of the light scattering coefficient ( $s$ ) and the light absorption coefficient ( $k$ ) require two different values of the reflectance factor at the particular wavelength, which may be values measured on a single layer (or sheet) over two different backgrounds, not necessarily a completely black and a very white background (Karipidis 1994). In this work, the reflectance factor measured on the assembly of quartz glass coated with the layer of the lowest coat weight over a black or white backing was used as “background”-value in the calculations (Figure 6). The sample, coated with a thicker layer of the same coating colour was then measured over a black and a white background. This means that effectively  $s$  and  $k$  were estimated for a “coating layer” of a coat weight corresponding to the difference between the thicker coating of the sample and the thin coating on the glass used as background. This was done to decrease the possible geometric effects of measuring a background covered by a glossy glass surface, while the coated sample has a less glossy surface and scatter light more diffusely.



**Figure 6.** Definition of “background” and “sample” in the calculations of  $s$  and  $k$  values.

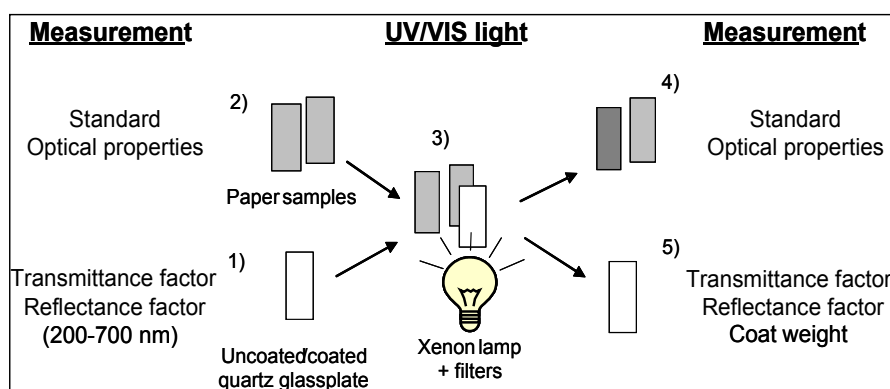
Using this approach,  $s$  values were determined over the spectrum. At shorter wavelengths, the calculations did not give correct values, probably because of too strong absorption (see e.g. Rundlöf, Bristow 1997). A linear extrapolation was therefore made from data at longer wavelengths, and the  $s$  values in the UV-region could be estimated. These approximate  $s$  values were used to calculate the corresponding values of  $k$  together with the calculated  $R_{\infty}$ , which was similar to the measured values since the background has little or no effect in the case of strong absorption (cf. Figure 18, section 4.2.1).

Calculations of  $s$  and  $k$  values were also made from transmittance factors measured using the integrating sphere and reflectance factors over the black background. Here, the presence of the quartz glass was ignored, and the measured values were used directly. Calculations were made at one wavelength, 350 nm, using the equations given by Karipidis (1994 and references therein). The equation

for the calculation of the transmittance factors at different coat weights from values of  $s$  and  $k$  are derived from the same source.

### 3.5 A method for studying coating layers and their influence on base paper (Paper III)

A method for studying the transmittance/reflectance of UV-radiation through thin coating layers in relation to their photo-stabilising properties was developed. The setup of the new method is shown in Figure 7 below.



**Figure 7.** A schematic description of the developed method.

The advantage of this developed method is the many possibilities for combining the different steps, as indicated by #1-5 in Figure 7.. The ageing characteristics of paper are determined by measuring the optical properties of paper samples before and after accelerated ageing with a xenon lamp (#2-4 in Figure 7). The ageing characteristics of a coating layer are determined by measuring the transmittance/reflectance factor ( $T_F/R_F$ ) between 200-700 nm, of a coated quartz glass plate before and after accelerated ageing with a xenon lamp (#1, #3 and #5 in Figure 7). When studying the influence of the UV-screening properties of a coating layer on a base paper all the steps (#1-5) are employed. The base paper sample is attached to the coated side of the quartz glass plate using tape, and is then placed in the accelerated light-induced ageing equipment with the quartz glass plate facing the xenon lamp (#3 in Figure 7). A reference base paper sample is also aged at the same time with no quartz plate in front of it. For more detailed information on the different steps, see Paper III. The developed method can also be applied when using an light-induced ambient ageing procedure.

## **4. RESULTS AND DISCUSSION**

*This chapter begins by presenting the results from the light-induced discolouration of different types of high-yield pulps during accelerated and long-time ambient ageing. Next, the development of the new method for studying the UV-screening effect of coating layers and their influence on base papers is discussed in some details, and this is followed by the results of the determination of the UV-screening properties of coating layers using this method. The final section part demonstrates the coating layers ability to protect birch CTMP against photo-discolouration.*

### **4.1 Light-induced discolouration of different types of high-yield pulps from a variety of wood raw materials (Papers I and II)**

To assess the photo-ageing characteristics of different types of high-yield pulps, a number of hand-made sheets were made and aged under both ambient and accelerated ageing conditions. There were great differences between the chosen ageing methods in the amount of UV-radiation present, the total light intensity reaching the exposed samples and the spectral distribution of the emitted light (cf. Figures 5a–b). The proposed ISO standard (N 1692) recommends xenon lamps with filters that mimic indoor daylight when performing accelerated light-induced ageing studies. The ASTM standard (D6789-02e2) also recommends xenon lamps during accelerated ageing.

The amount and intensity of UV-radiation present in a normal office environment is very low (Jordan, O'Neill 1991; McGarry et al. 2004). Therefore, the use of solely artificial light with the right spectral characteristics (e.g., fluorescent lamps) is a realistic way to model indoor photodiscolouration, since no indirect daylight is needed (McGarry et al. 2004). Thus the fact that no daylight reached the paper samples in the long-term ambient ageing setup should not influence the results obtained when simulating an office environment, a fact which facilitates the ambient light-induced ageing procedure.

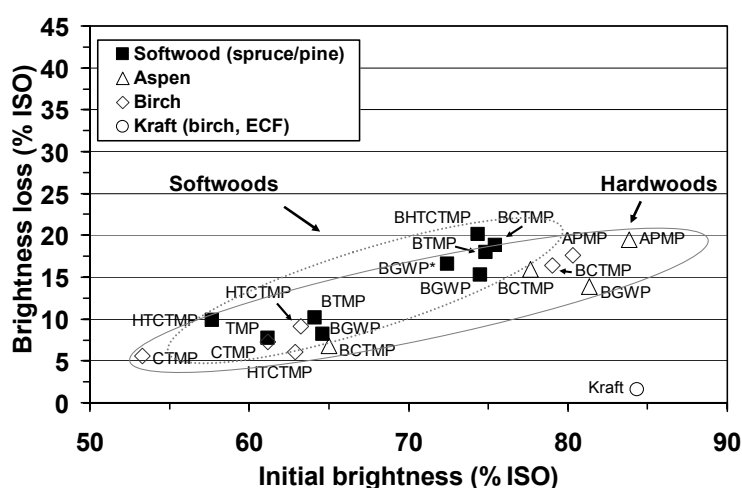
Information regarding the brightness, bleaching chemicals used, and lignin and extractive contents of the studied pulps prior to ageing are presented in Table 3 (cf. section 3.1). Figures 8 to 11 show the brightness reversion of a large number of high-yield pulps that were aged according to the two procedures described in section 3.2.

#### **4.1.1 Effect on brightness**

During light exposure, a bleached pulp loses more brightness units than an unbleached pulp (see section 2.4 and Figures 8–11). This is an expected behaviour, and is partly a consequence of the Kubelka–Munk relationship (brightness is not linearly related to the chromophore content) and partly a consequence of the

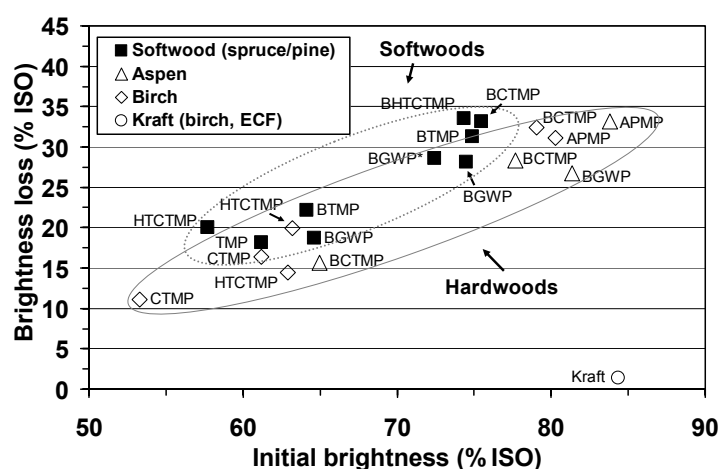
generation of light-sensitive structures during lignin-retaining bleaching (Forsskähl 2000). Hence, it is only relevant to compare paper samples with approximately the same initial brightness, when discussing differences in brightness reversion between different types of pulps. Nevertheless, it is possible to make comparisons of the photo-degradation characteristics of different pulps in the same brightness range when presenting the results in the form used in Figures 8 to 11. Moreover, since brightness is the optical property most frequently used in the paper industry when describing the appearance of a paper, it is of special interest to follow the loss in brightness during ageing.

Figure 8 shows the extent of brightness reversion after 4 hours of accelerated light-induced ageing. The rather intense ageing conditions were enough to cause severe discolouration of up to 20 ISO brightness units for the pulps with the highest brightness despite the very short period of ageing time. However, these results imply that regardless of the pulping process used, hardwood pulps are somewhat more photo-stable compared to softwood pulps (cf. section 2.4.1). The difference is most prominent in the high-brightness range. Neither bleaching method (sodium dithionite or hydrogen peroxide) nor pre-treatment procedure (sulphite or alkaline hydrogen peroxide) influenced the photo-stability measured as brightness loss to any significant extent. Groundwood pulps though, seem to be somewhat more photo-stable compared to refiner mechanical pulps, at least at higher brightness levels.



**Figure 8.** Brightness loss after accelerated light-induced ageing for 4 hours 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 2. BGWP\* contains 26% pine and 8% poplar; the rest is spruce.

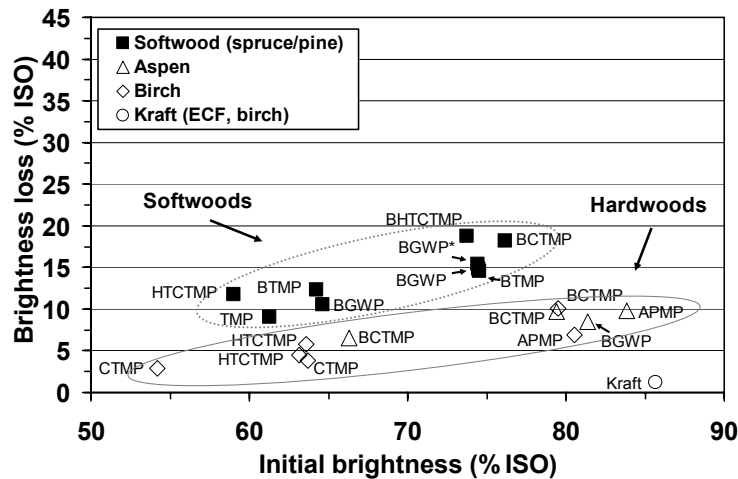
Figure 9 shows the extent of brightness reversion after 24 hours of accelerated ageing. A comparison of the results presented in Figures 8 and 9 reveals that extending the time of irradiation made the hardwood pulps become somewhat more distinct from the softwood pulps. These findings support the previous conclusion that hardwood high-yield pulps are somewhat more photo-stable compared to softwood high-yield pulps. In total, lengthen the time of accelerated ageing to 24 hours did not change the general conclusions predicted after accelerated ageing for a shorter period of time (4 hours).



**Figure 9.** Brightness loss after accelerated light-induced ageing for 24 hours 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 2. BGWP\* contains 26% pine and 8% poplar; the rest is spruce.

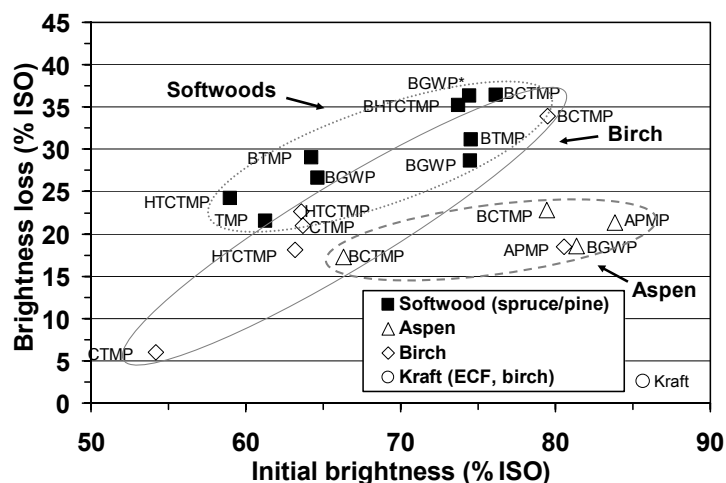
Figure 10 shows the results of ambient light-induced ageing for 20 weeks. The hardwood pulps respond quite differently to this low-intensity ageing than subjected to accelerated light-induced ageing. They were much more photo-stable throughout the 20-week low-intensity ageing period, especially in the high-brightness range. This result means that predictions based on accelerated ageing are likely to overestimate the extent of brightness reversion of hardwood high-yield pulps. The ageing characteristics of the softwood pulps, however, regardless of the high-yield pulping method employed were rather similar for both accelerated and long-term ambient light-induced ageing, (cf. Figures 8 and 10). Thus, when performed as described in this study, the two ageing methods provide comparable results for softwoods; 4 hours of accelerated light-induced aging corresponds to about 20 weeks of ambient light-induced ageing, and 24 hours of

accelerated light-induced ageing corresponds to approximately one year of ambient light-induced ageing.



**Figure 10.** Brightness loss 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 2. BGWP\* contains 26% pine and 8% poplar; the rest is spruce.

Extending the ambient light-induced ageing to one year revealed dissimilar behaviour among the hardwood pulps (Figure 11). Regardless of the high-yield pulping process used and the initial brightness, the brightness loss for aspen pulps was much lower than that for softwood and birch pulps. In addition, the degree of darkening of a birch pulp approached that of a softwood pulp (cf. Figure 11). In other words, the birch high-yield pulps used in this study will only temporarily outperform a softwood high-yield pulp. Therefore, aspen-based pulps are to prefer when producing long-life high-quality paper grades. There is, however, one exception: the birch alkaline peroxide mechanical pulp (APMP) showed a brightness loss similar to that of aspen pulps, probably due to the lower lignin content (cf. Figure 13) due to the lower yield of the APMP process (compared to other mechanical pulping processes).



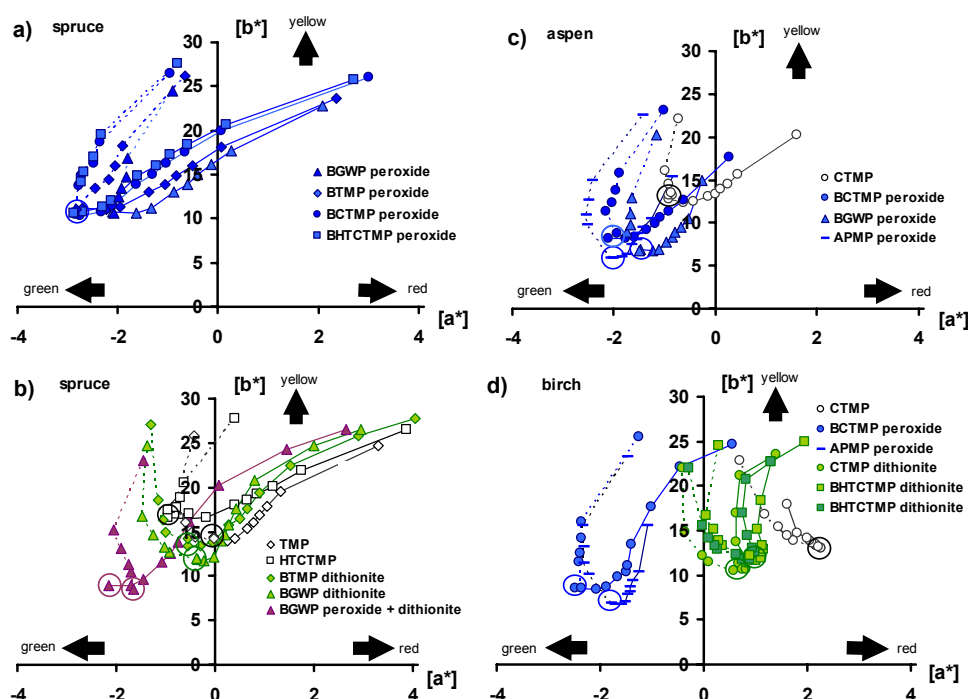
**Figure 11.** Brightness loss after long-term light-induced ambient ageing for one year for different types of high-yield pulps. The ageing characteristics of an ECF-bleached birch kraft pulp are given as a reference. Abbreviations used in the figure can be found in Table 2. BGWP\* contains 26% pine and 8% poplar; the rest is spruce.

There are several possible explanations for the observed differences between the softwood and hardwood pulps. Hardwoods contain approximately 20–25% lignin by dry weight, while softwoods contain somewhat more; 26–32% lignin. Moreover, the lignin structure differs between hardwoods and softwoods. The lignin in hardwoods is a syringyl-guaiacyl lignin, while the lignin in softwoods is guaiacyl lignin (Sjöström 1993). Because lignin is an efficient absorber of UV-radiation, the amount and structure of lignin will most likely influence the degree of absorption, and thereby the irradiation-induced discolouring characteristics of a pulp. The variations in absorptivity at different wavelength regions will affect both the discolouring tendencies and the photo-bleaching ability of a high-yield pulp.

#### 4.1.2 Effect on colour (CIE $L^*$ , $a^*$ and $b^*$ )

Figures 12a–d show the change in colour (cf. section 2.4.2) of the same high-yield pulps that were used in the study that is discussed above. The general effect of ageing was darkening of the pulp (due to stronger light absorption, especially at short wavelengths), meaning that the  $L^*$  coordinate decreased upon ageing in a rather similar way for all pulps. Therefore only the  $a^*$  and  $b^*$  coordinates were chosen to represent the change in colour in Figures 12a–d. Since the ageing behaviour of high-yield pulps produced from hardwoods differed over time, an ambient ageing period of up to 52 weeks was chosen to fully elucidate their behaviour (see section 4.1.1 and Paper I). Comparable results from accelerated

ageing were obtained after 24 hours for most chemimechanical and mechanical pulps produced from spruce and birch. Note the different scales on the  $a^*$  and  $b^*$ -axes in Figures 12a–d. The paper sheets were generally more prone to move towards yellow (an increase in  $b^*$  value) in the  $a^*$ - $b^*$  diagram, but there was also a significant change in  $a^*$  value (green/red) for most pulps. However, the comparatively small increase in the  $a^*$  coordinate was clearly visible to the human eye as a more reddish appearance of the sheets.



**Figures 12a-d.** Discolouration of mechanical and chemimechanical pulps a), b) spruce, c) aspen and d) birch monitored over 52 weeks of ambient ageing (solid lines) and 24 hours of accelerated ageing (broken lines). The circled symbols represent the starting points (i.e., unaged paper sheets). The abbreviations used in the figure can be found in Table 2.

The change in colour of high-yield pulps during light-induced ageing was dependent on the conditions of ageing. Mechanical and chemimechanical pulps from spruce reach almost the same value on the  $b^*$ -axis regardless of the ageing methods (and bleaching processes) used; see Figures 12a and 12b. This is in accordance with the previous results regarding the brightness loss of the same paper sheets (see Figures 8-11). The accelerated light-induced ageing method had more or less the same impact on all mechanical and chemimechanical pulps studied. The value of  $b^*$  increased (more yellow, cf. Figures 12 a-d) and the value of  $L^*$  decreased as expected.

The change in  $a^*$  value on the other hand, was influenced by the bleaching chemical used. Hydrogen peroxide bleached pulps first showed no change, or a slight decrease in  $a^*$  value followed by an increase, giving an overall small increase in  $a^*$  (i.e., a colour shift towards red). For the hydrogen peroxide bleached softwood and hardwood pulps, the increase in the  $a^*$  coordinate was in the range of 1.2–2.2 and 0.3–1.1, respectively. Dithionite bleached pulps instead showed a small decrease in  $a^*$  value (i.e. a slight shift towards green). Unbleached spruce TMP and unbleached birch CTMP display the same behaviour as the dithionite bleached pulps. The  $a^*$  value of unbleached spruce HTCTMP increased by 0.92, and that of unbleached aspen CTMP by 0.12. The discolouration was mainly caused by the pulps turning darker and more yellow, but a smaller but significant change towards red, or, in some cases, green, was also observed.

The ambient light-induced ageing method revealed three different ageing profiles depending on whether the high-yield pulp was produced from spruce, aspen or birch wood. Bleached hardwood high-yield pulps showed a smaller change in  $a^*$  value (0.6–3.0), birch pulps in particular (Figure 12d) compared to the spruce pulps in Figures 12a and 12b (3.3–5.8). Aspen pulps displayed the smallest change in  $b^*$  value (Figure 12c).

Like the spruce mechanical and chemimechanical pulps, the birch pulps had different colour before ageing, depending on the bleaching method used, but they also had different colour at the end points as well. Moreover, the behaviour of the  $a^*$  value over time for birch was different from that for spruce and aspen. At first, the  $a^*$  value increased with time; then there was a phase in which it was nearly constant; and at the end, after about 30 weeks of ambient ageing, it increased again, giving the paper a both measurable and visible reddish hue.

Figure 12c show that the  $b^*$  values after ambient ageing did not reach the same level as the  $b^*$  values after accelerated ageing for the aspen pulps. This is in agreement with the measured brightness loss (cf. section 4.1.1) where the darkening tendencies of hardwood high-yield pulps (especially aspen pulps) were shown to be overestimated when using an accelerated light-induced ageing procedure. There was one exception, however, the unbleached aspen CTMP, which reached about the same value of  $b^*$  with both accelerated and ambient ageing. One explanation for this discrepancy might be that the unbleached aspen CTMP had an initial ISO brightness of 66%, while the hydrogen peroxide bleached aspen pulps all had an initial brightness of at least 78% ISO.

The mechanical pulping process seemed to have only a minor impact on the colour change during ageing of both softwood and hardwood pulps, although there were a few exceptions. Groundwood pulps were slightly more stable, independently of bleaching method. Pulps produced from aspen behaved the same regardless of how they were processed, although, it might be possible to identify a slight increase in  $a^*$  value (slightly more red) for the CTMP samples. The birch

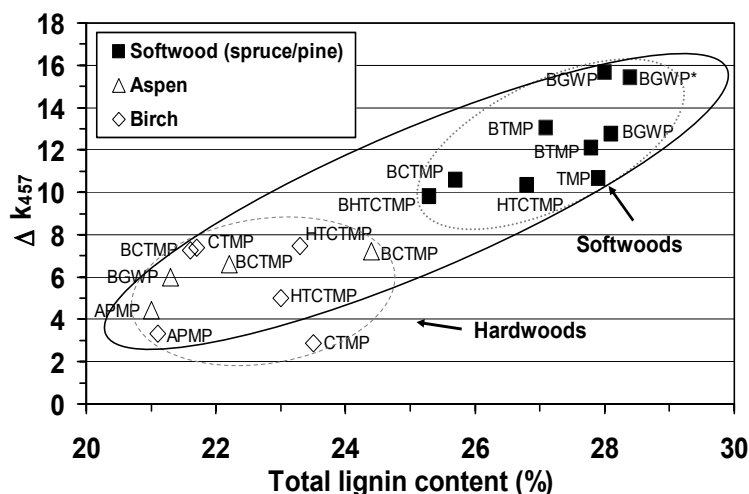
APMP was distinct from the other birch pulps. Its behaviour was more like that of the aspen pulps, and displayed a smaller change in  $b^*$  value, they also lacked the increase in  $a^*$  value at the end of the ambient ageing period. Regardless of the wood raw material used, the alkaline peroxide mechanical pulps showed the smallest change in colour despite having had the highest initial brightness.

It is evident from this investigation that high-intensity accelerated and low-intensity ambient light-induced ageing generate either different types of chromophores or different compositions of chromophores as indicated by differences in the CIE  $a^*$  and  $b^*$  values obtained. This underscores the importance of using the right experimental set-up when evaluating the mechanism of light-induced ageing or the photo-stability of untreated, additive-treated or chemically modified high-yield pulps. Using the right ageing method is also important when choosing the proper mechanical or chemimechanical pulp for a particular end-product.

#### **4.1.3 Influence of lignin content**

Lignin is an efficient UV-absorber, and has been attributed as the main cause of the rapid light-induced discolouration of high-yield pulps (see section 2.4). The light absorption coefficient,  $k$ , is proportional to the amount of chromophoric substances which are responsible for the discolouration, and is therefore a valuable tool for evaluating the influence of lignin content on light-induced discolouration. When investigating the relationship between lignin content and light-induced yellowing, long-term ambient ageing was used since the accelerated ageing method had been shown to give unreliable values for aspen pulps (cf. sections 4.1.1 and 4.1.2).

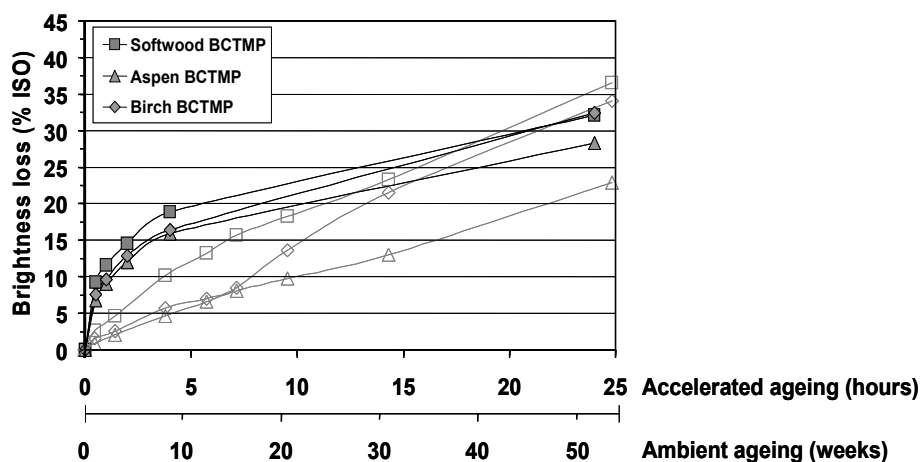
Figure 13 shows the degree of discolouration (measured as  $\Delta k_{457}$ ) as a function of the total lignin content of the pulps. It is obvious that there exists a strong correlation between lignin content and the degree of discolouration, regardless of the wood raw material or the pulping or bleaching method used.



**Figure 13.** The extent of photo-yellowing ( $\Delta k_{457}$ ) 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 2. BGWP\* contains 26% pine and 8% poplar; the rest is spruce.

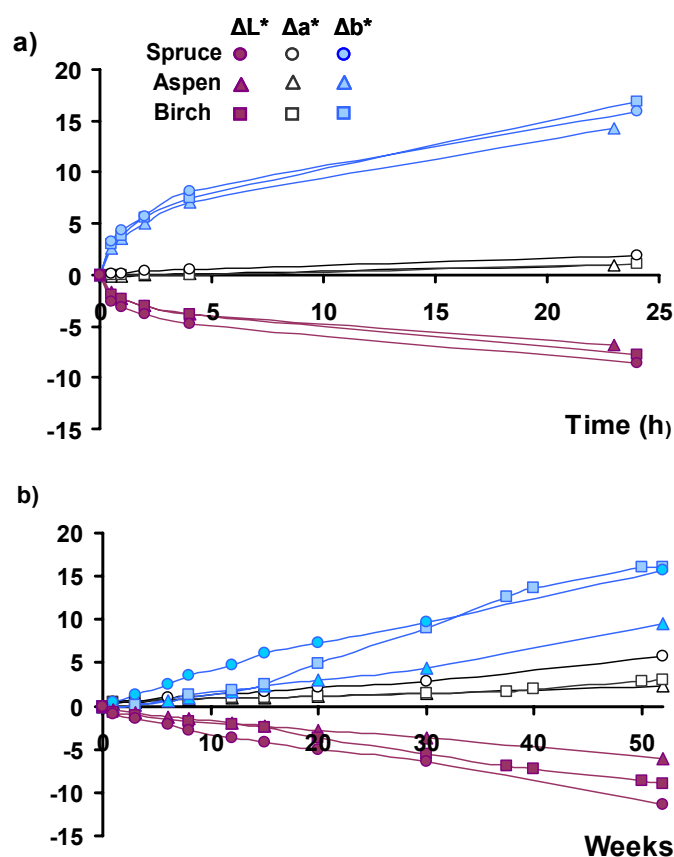
#### 4.1.4 General comments on the different ageing procedures

Figure 14 shows the brightness loss of three chemithermomechanical pulps as a function of irradiation time for both accelerated and ambient ageing conditions. The three pulps are spruce, birch and aspen CTMP, all of which were hydrogen peroxide bleached to about the same initial brightness level (76-79% ISO). The results from ageing of the CTMPs can also be found in Figures 8–13. It has been shown that light-induced discolouration is characterised by a rapid initial phase followed by a slower less detrimental phase (cf. discussion in section 2.4.3). The transition between the initial and secondary phase occurs somewhere between an irradiation time of 2-4 hours when performed under the accelerated ageing conditions used in this work. It is interesting to notice that the initial phase for the low-intensity ambient ageing conditions was less pronounced and also that the birch CTMP approached the spruce CTMP at extended periods of long-term ambient light-induced ageing. As seen in Figure 14, brightness loss after accelerated light-induced ageing for 4 hours was 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 was performed as described in the experimental section (of this thesis).



**Figure 14.** 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 initial brightness of the chemithermomechanical pulps was in the range of 76-79% ISO.

Figures 15a–b show the results of using the CIELAB colour system to describe the behaviour of the spruce, birch and aspen CTMPs when subjected to accelerated or long-term ambient light-induced ageing. As previously noticed (see section 2.4.3), the initial phase is not very pronounced when high-yield pulps are aged under ambient conditions with no indirect sunlight present (Figure 15b). When using the accelerated ageing procedure, the two ageing phases could clearly be seen in the  $b^*$  and  $L^*$  values (Figure 15a). The long-term ambient ageing method revealed diverse appearances depending on the wood raw material. For spruce, the change in  $L^*$ ,  $a^*$  and  $b^*$  values was nearly linear. Over the first 1–2 weeks the discolouration of the spruce pulps was due to an increase in  $a^*$  value (cf. Figure 12b) while the  $b^*$  value remained constant. The aspen and birch CTMPs showed no change in  $b^*$  value for the first three weeks. This period was followed by a small linear increase in the  $b^*$  coordinate which continued until week 15 (birch) and week 30 (aspen), after which the increase in  $b^*$  value became slightly more pronounced, especially for the birch CTMP. It may therefore be somewhat misleading to think of light-induced ageing as pure yellowing; indeed on the time scale of a few weeks the pulp may become more reddish before any pronounced increase in yellowness begins.



**Figures 15a-b.** The change (aged - unaged) in CIE  $L^*$ ,  $a^*$  and  $b^*$  values of hydrogen peroxide bleached spruce, aspen and birch CTMP during a) accelerated light-induced ageing and b) long-term ambient light-induced ageing. The CTMPs are the same pulps as used before (Figure 14). The initial brightness of the CTMPs was in the range of 76–79% ISO.

There have been numerous proposals made regarding the type of chromophores that are formed during light-induced ageing of lignocellulosic materials (see section 2.4.4.3). The chemical composition of mechanical or chemimechanical pulp depends mainly on the fibre source (e.g., softwood or hardwood species), but also to a lesser extent on the production method (e.g., fibre separation and bleaching processes). Both of these will influence the extent of discolouration. Furthermore, the ageing method itself will be of utmost importance concerning the formation of coloured substances as shown in Paper II.

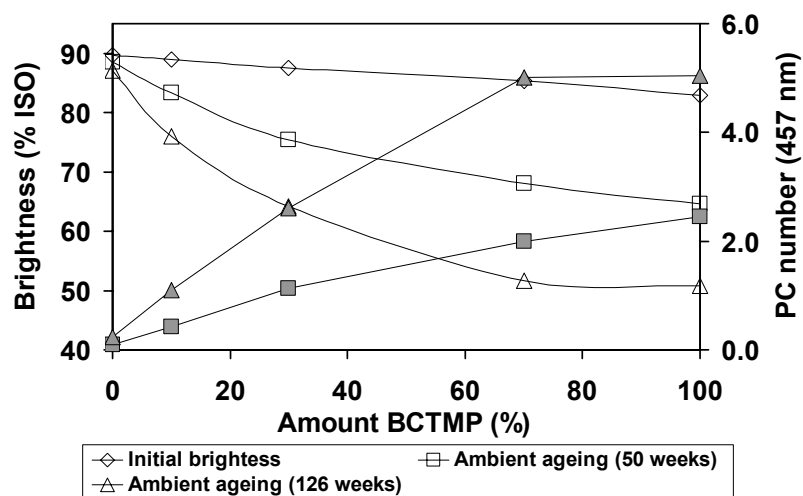
It is evident from this study that high-intensity accelerated and low-intensity ambient light-induced ageing generate either different types of chromophores or different compositions of chromophores as indicated by differences in the CIE  $a^*$

and  $b^*$  values obtained. Ambient ageing tends to generate coloured substances that have absorption at higher wavelengths than the chromophores generated during accelerated ageing. This finding highlights the importance of using the right experimental set-up when evaluating the mechanism of light-induced discolouration or the photo-stability of untreated, additive-treated or chemically modified high-yield pulps. Using the proper ageing method is also important when choosing a suitable mechanical or chemimechanical pulp for a particular end-product.

#### **4.1.5 Effect of substituting chemical pulp with birch CTMP**

Figure 16 shows the brightness values before and after ambient light-induced ageing of paper sheets containing various amounts of hydrogen peroxide bleached birch CTMP. The degree of brightness reversion is expressed as the post-colour (PC) number (Giertz 1945); PC number offers a way of partly circumventing the problem posed by different initial brightness values.

Substituting parts of the furnish with birch CTMP progressively decreased the initial brightness of the furnish as the amount of bleached birch CTMP increased. As can be seen in Figure 16, even small amounts of birch CTMP in the furnish cause severe brightness reversion. This is result in agreement with the findings of Paulsson and Parkås (2001) who reported a vital decrease in photo-stability when small amounts of hydrogen peroxide bleached spruce CTMP were added to papers containing an admixture of hydrogen peroxide bleached spruce CTMP and softwood ECF-bleached kraft pulp. The major loss in brightness was seen when the first amounts of birch CTMP were added. The discolouration (measured as PC number) increased linearly up to the point where BCMTP constituted about 70% of the furnish, after which the curves began to flatten.



**Figure 16.** ISO brightness (unfilled symbols) and PC number (filled symbols) as a function of the amount of birch BCTMP in a furnish. The papers were subjected to long-term ambient ageing for 50 and 126 weeks.

#### 4.1.6 The best choice of high-yield pulps for long-life paper and paperboard products

Apparently, mechanical and chemimechanical pulps will lose brightness and suffer from light-induced discolouration no matter how they are produced. The only difference relates to how rapidly the degradation will occur. When it comes to raw material, hardwood high-yield pulps (especially aspen pulps) are more photo-stable compared to softwood pulps. Hardwood pulps should therefore be the first choice for applications where a high permanence is desirable.

## 4.2 Developing a method for evaluating the photo-yellowing of coated papers (Paper III)

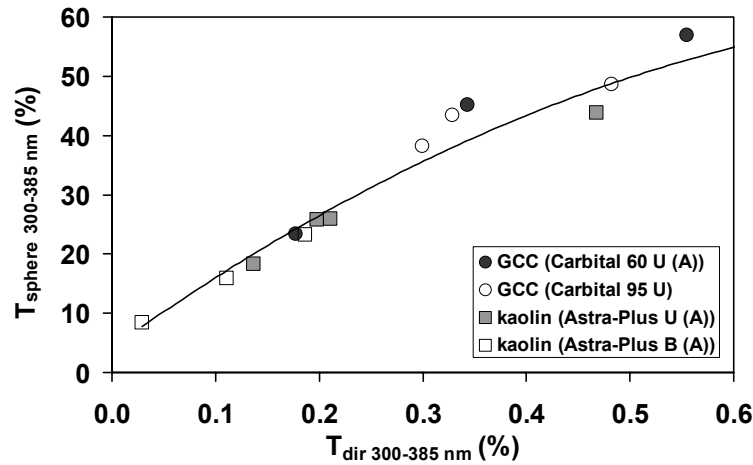
A number of problems must be overcome in order to study coating layers, and their influence on brightness stability of a base paper. High-yield mechanical or chemimechanical pulps have high surface roughness and high water absorption ability, which often leads to uneven surface coverage at low coat weights. Another dilemma that arises when studying a coated paper is that it is impossible to distinguish changes caused by discolouration of the coating layer from changes caused by discolouration of the base paper. These problems are addressed in the developed method by the use of coated quartz glass plates, enabling the coat weight and the reflectance and transmittance properties of the coating layer to be measured on exactly the same coated area. Very thin and uniform coating layers

can be deposited on these plates. The experimental procedure has the further advantage that it is fast and simple.

#### 4.2.1 Measurement of transmittance of coating layers

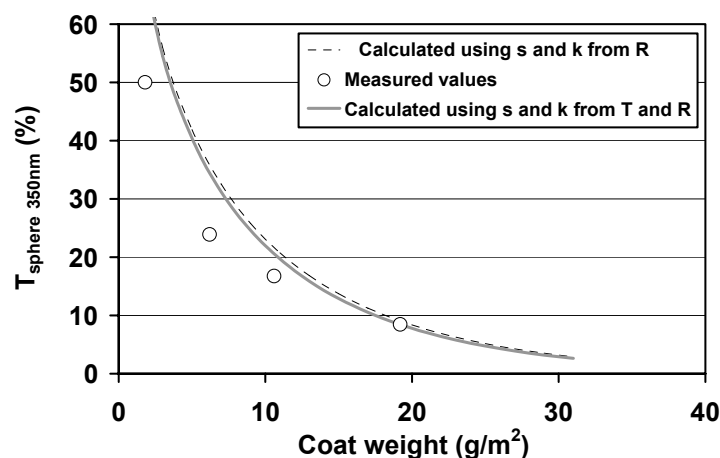
Quartz glass is also highly transparent in the UV-region of the spectrum, and the optical properties of the plates are easily measured, and can be compensated for to estimate the transparency of the coating layer as such from data measured on coated glass. The coated samples were illuminated at  $0^\circ$  to the normal of the surface by a beam of light and the wavelength of the illumination was scanned over the UV-VIS spectrum. Two geometries for detecting the transmitted light were tested: i)  $0^\circ/d$ , an integrating sphere placed behind the sample, which collects most of the light transmitted in all directions and ii)  $0^\circ/0^\circ$ , using the detector of the spectrophotometer placed behind the sample, directly opposite to the light source, collecting transmitted light only at narrow angles to the normal of the surface. For more detailed information about the two measuring geometries, see section 3.4.

Figure 17 shows a comparison between the two methods, the values presented are a mean of the data collected in the UV-region between 300 and 385 nm in wavelength. As expected, the transmittance factors obtained using the integrating sphere ( $0^\circ/d$  geometry),  $T_{sphere}$ , were much higher than those measured in the direction of the illumination only ( $0^\circ/0^\circ$  geometry),  $T_{dir}$ , where the diffusely transmitted light was excluded. There was however a good correlation between them, showing that the transmittance factor measured in the direction of the illumination can be used to represent the overall transmittance of the samples at least for the investigated range of coat weights (2-27 g/m<sup>2</sup>). Because of this, straightforward measurement using a single beam ( $0^\circ/0^\circ$  geometry) was chosen for the first study (sections 4.2.1-4.2.3).



**Figure 17.** Mean transmittance factors in the UV-region between 300-385 nm, obtained using an integrating sphere for detection of the diffusely transmitted light,  $T_{sphere}$ , ( $0^\circ/d$  geometry) and by detecting the transmitted light directly opposite to the illumination at narrow angles to the normal of the sample,  $T_{dir}$ , ( $0^\circ/0^\circ$  geometry). For information of the pigments see Tables 4 and 5.

An attempt was made to estimate the light scattering and light absorption coefficients,  $s$  and  $k$ , of a coating layer in the UV-region of the spectrum. This was done in two ways: from the measured reflectance factors over a black and a white background and from the transmittance factors obtained using the sphere. For one of the clay coatings shown in Figure 17 (Astra-Plus B,  $19.2 \text{ g/m}^2$ ), the  $s$  value at 350 nm was estimated to  $225 \text{ m}^2/\text{kg}$  (from reflectance data) and  $240 \text{ m}^2/\text{kg}$  (using transmittance data in addition), the corresponding  $k$  values were 19.5 and 19.3  $\text{m}^2/\text{kg}$  respectively. The  $s$  values are in fair agreement with those reported by Karipidis (1994) for a clay coating, considering the fact that  $s$  increases with decreasing wavelength, and that different instruments and sample preparations were used. The values of  $k$  were higher than those normally obtained at visible wavelengths, which is probably due to that many materials absorb UV-radiation to a higher extent than visible radiation. Thus, it seems to be possible to get reasonable estimations of  $s$  and  $k$  in the UV-region from these data. These  $s$  and  $k$  values were used as a starting point to calculate the transmittance factor as a function of coat weight using the Kubelka-Munk equations (*ibid.*). Figure 18 shows the calculated relations (solid and broken lines) and the measured transmittance factors using the sphere (open symbols). Despite the fact that several approximations were involved in estimating  $s$  and  $k$  from the reflectance data, there is a good agreement between measurement and calculation at  $19 \text{ g/m}^2$ . Further, this experimental curve, and the other measured values presented, shows the same non-linear shape as the calculated curves.

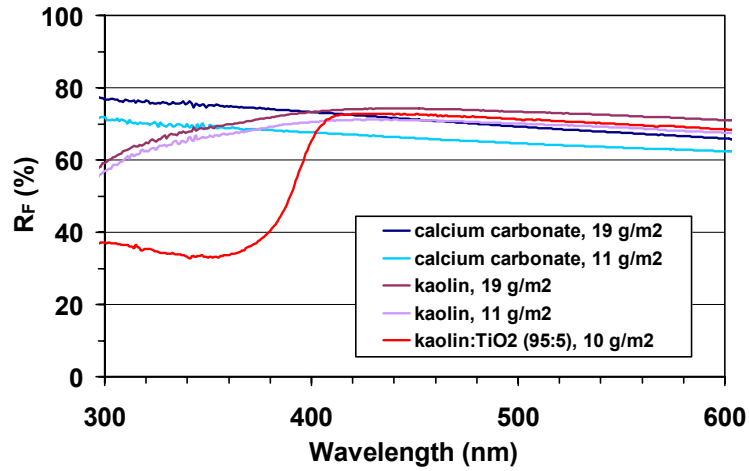


**Figure 18.** Calculated and measured values of the transmittance factor at 350 nm as a function of coat weight for one of the clays [Astra-Plus B (A)]. The measurements were conducted using the 0°/d° geometry setup. For information of the pigment see Table 4.

Deviations of measured values from the calculated values at low coat weights has been observed and discussed by e.g. Karipidis (1994). When calculating  $s$  and  $k$  for coatings, the values often seem to change with coat weight, especially in the lower range, so that the agreement could probably be improved if  $s$  and  $k$  were determined separately for each coat weight. This is however beyond the scope of this work.

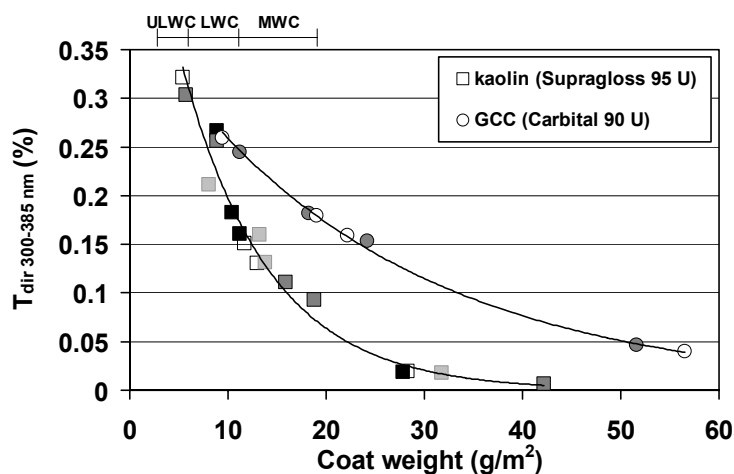
#### 4.2.2 Repeatability of the transmittance measurements

The reflectance factor of coated quartz glass was measured at different wavelengths between 300–600 nm over a white background. The results for ground calcium carbonate (GCC), kaolin and kaolin/TiO<sub>2</sub> (95:5) coatings at different coat weights are presented in Figure 19. As seen in the figure, the GCC and kaolin pigments reflect around 60–80% of the incoming light. The reflectance factor for kaolin, as compared to GCC, was somewhat higher in the visible region but lower in the UV-region. For kaolin/TiO<sub>2</sub> (95:5), the reflectance factor was much lower in the UV-region compared to GCC, as previously reported (Johnson 1991). This phenomenon is most likely due to the higher light absorption ability of the kaolin and the TiO<sub>2</sub> pigments (Bown 1997). High ability to absorb radiation in the UV-region also implies low transmittance in the same region; in case of TiO<sub>2</sub> the high light scattering ability will have further contributes to a low transmittance.



**Figure 19.** Reflectance factors of different pigments applied as coatings onto quartz glass plates measured over a white background in the wavelength region 300–600 nm. The order in the legend matches the order in which the pigments appear on the left-hand side of the figure. The pigments used were Supragloss 95 U (kaolin) and Carbital 90 U (calcium carbonate). For information of the pigments see Tables 4 and 5.

Figure 20 shows the transmittance factor  $T_{dir}$  (300–385 nm) for coatings made of kaolin or GCC at different coat weights. As a consequence of the chosen experimental method, very low absolute transmittance values were obtained in the UV-region (below 0.5%). The strong dependence of the coat weight, especially for very low coat weights, was in accordance with the predictions of the Kubelka-Munk equations for transmittance (cf. Figure 18). The UV-region 300–385 nm was chosen according to the earlier discussion in section 2.4.



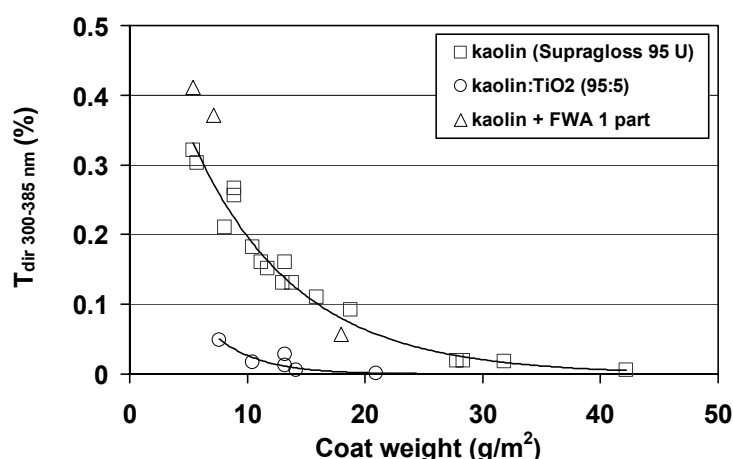
**Figure 20.** Transmittance factor,  $T_{dir}$ , in the 300–385 nm region of coating colours containing kaolin (Supragloss 95 U) or ground calcium carbonate (Carbital 90 U) pigments. To evaluate the repeatability, the experiments were performed on four different occasions, represented by the unfilled, lightly or darkly shaded or filled symbols. ULWC = ultralight weight coated (~4–7 g/m<sup>2</sup>); LWC = light weight coated (~7–12 g/m<sup>2</sup>); MWC = medium-weight coated (~13–20 g/m<sup>2</sup>). The measurements were conducted using the 0°/0° geometry setup. For information of the pigments see Tables 4 and 5.

In order to evaluate the repeatability of the method, transmittance measurements were made on several different occasions, with a new coating colour being prepared each time. The results from these measurements are presented in Figure 20; and as can be seen, the deviations were small, even in the ULWC and LWC regions. The repeatability of the developed model system is therefore satisfactory.

#### 4.2.3 The new method to measure the inhibition of photo-discolouration from coating layers

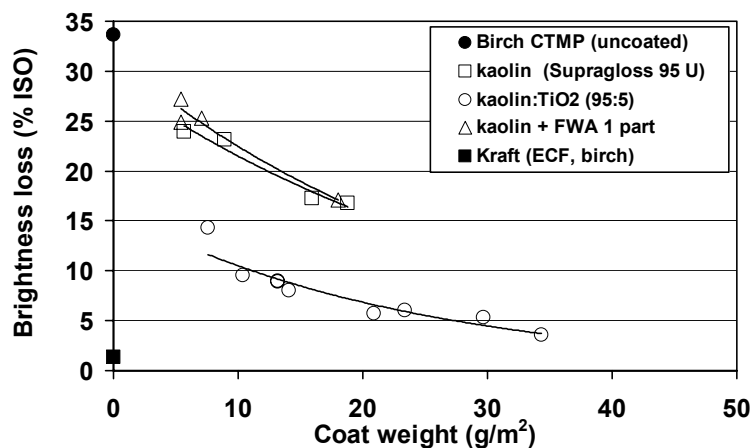
As previously mentioned, hardwood high-yield pulps have been shown to be more photo-stable than softwood high-yield pulps, and are therefore the preferred alternative for replacing some of the chemical pulp in a furnish or high-quality paper grades such as fine paper. A base paper consisting of 100% hydrogen peroxide bleached birch CTMP was therefore used in the investigation of the protective abilities of different coating formulations. The results of this investigation are presented in Figures 21 and 22. The transmittance factor in the UV-region 300–385 nm for coating colours containing kaolin clay and different additives is shown in Figure 21. As expected on the basis of previous research (Fossum et al. 1976; Gellerstedt et al. 1983; Johnson 1989, 1991; Ghosh et al. 2002), a small substitution of kaolin with TiO<sub>2</sub> (5 parts) lowered the transmittance factor considerably. Adding a fluorescent whitening agent (FWA) to the coating colour

seemed to increase the transmittance factor somewhat at low coat weights (<10 g/m<sup>2</sup>). In the coat weight region normally used in paper production (8–12 g/m<sup>2</sup>), the curves are steep, indicating the importance of obtaining an even coating layer. Hence, if coating is to be used as a tool to prevent light-induced brightness reversion, the major concerns are to obtain a smooth base paper, an appropriate coating colour formulation and coating procedure.



**Figure 21.** Transmittance factor,  $T_{dir}$ , in the 300–385 nm region of coating colours containing kaolin clay and the additives titanium dioxide (TiO<sub>2</sub>) and fluorescent whitening agent (FWA). The measurements were conducted using the 0°/0° geometry setup. For information of the pigments see Tables 4 and 5.

The same coating layers as in Figure 21 above were then placed in front of a base paper made of hydrogen peroxide bleached birch CTMP and subjected to accelerated light-induced ageing. Figure 22 shows the change in ISO brightness of the base paper after 24 hours of irradiation. As can be seen in the figure, the coating colour containing 5 parts TiO<sub>2</sub> (coat weight of ~12 g/m<sup>2</sup>) was effective in photo-stabilising the CTMP paper. The brightness loss decreased by roughly 75% compared to the uncoated base paper, and by roughly 50% compared to the kaolin-coated base paper. This reduction in brightness loss might be less than expected from the reduced transmittance factor but since the chromophores are formed via radical reactions (cf. sections 2.4.4.2 and 2.4.4.3); it only takes a small amount of UV-radiation to initiate the reactions. It should, also, be noted that only the transmitted radiation between 300 and 385 nm was accounted for. Other wavelengths may also contribute to light-induced brightness reversion.



**Figure 22.** Change in ISO brightness after accelerated light-induced ageing for 24 hours following the procedure described in Figure 7 (section 3.5). The ageing characteristics of uncoated hydrogen peroxide bleached birch CTMP and ECF-bleached birch kraft pulp are given as references. For information of the pigments see Tables 4 and 5.

Additionally, the choice of photo-ageing procedure may influence the outcome of the ageing experiment (Paulsson, Parkås 2001; Paper I and II). It was, however, evident that no substantial change in the transmission characteristics of the coating layers in the UV-region had occurred during ageing.

The addition of FWA did not improve photo-stability, at least not in the amounts used in this investigation. Previous research has reported that fluorescent whitening agents are capable of inhibiting the light-induced discolouration of lignin-containing papers (Bourgoing, Robert 1997; Bourgoing et al. 2001; Ragauskas et al. 2001). UV-radiation can, however, degrade the fluorescent whitening agent, thus rendering the paper darker with time (Rohringer, Fletcher 1996; Paulsson, Ragauskas 1998a). The relationship between the transmittance factor of the coating layers and the brightness loss of the underlying base paper is clearly evident when comparing Figure 21 and Figure 22.

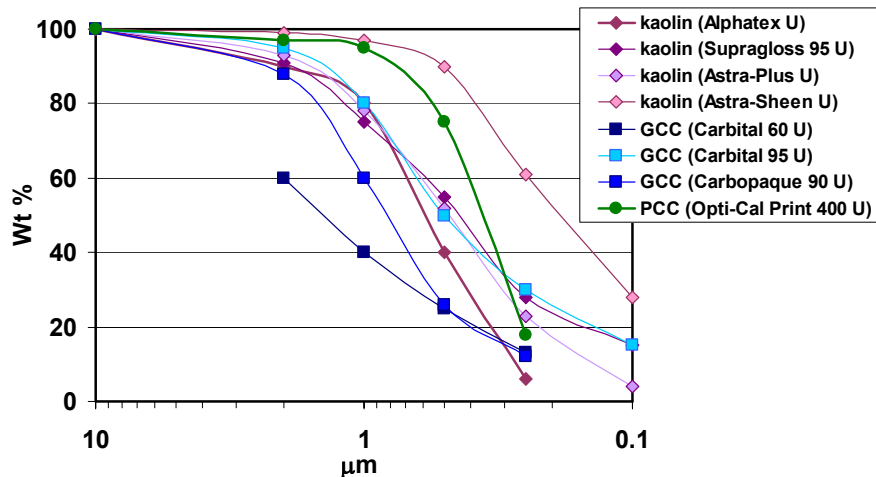
In conclusion, this study demonstrates the high repeatability of the developed method, even at low coat weights. Given this confirmation of the ability of the method to correlate the transmittance factor of coating layers with their photo-stabilising properties, the same method was used in the work presented below.

### 4.3 The UV-screening properties of coating layers (Paper IV and V)

The method described in sections 3.5 and 4.2 was used to investigate how pigment type, particle shape, particle size, particle size distribution, binders and UV-absorbing additives affect the UV-screening properties of coating colours.

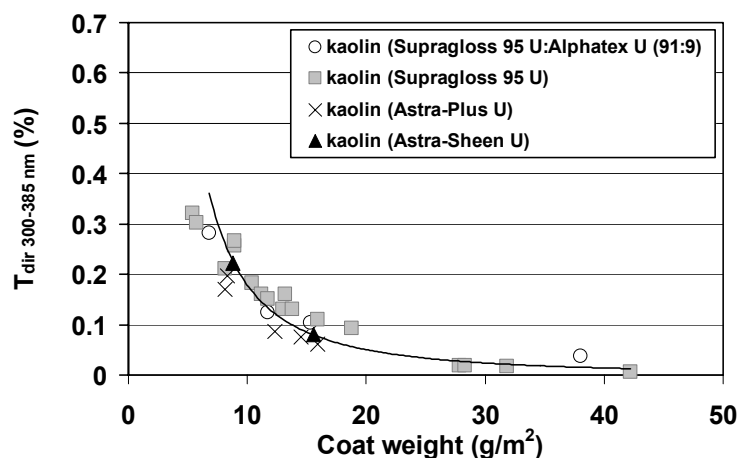
#### 4.3.1 Influence of coating pigments – Initial studies

Eight unbleached commercial available pigments with various particle shape, particle size, particle size distribution (psd) and light-scattering characteristics were examined. The pigments comprised four clays (Supragloss 95 U, Astra-Sheen U, Astra-Plus U and Alphatex U) and four carbonates (Carbital 60 U, Carbital 95 U, Carbopaque 90 U and Opti-Cal Print 400 U). More information about the pigments used can be found in Tables 4 and 5 and in Figure 23 below.

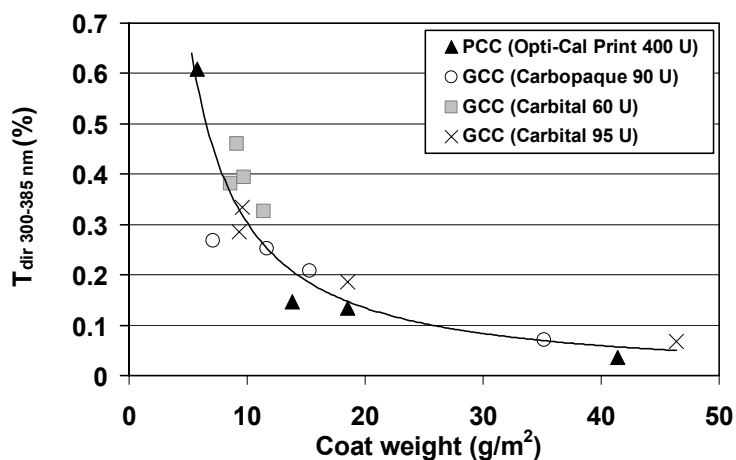


**Figure 23.** Pigment size distribution for the kaolin and calcium carbonate pigments. For information of the pigments see Tables 4 and 5.

Figures 24 and 25 show the transmittance factor,  $T_{dir}$ , in the 300–385 nm region of coating colours containing the above named kaolin or calcium carbonate pigments. A comparison of the results in Figures 24 and 25 reveals that kaolin pigments display a somewhat lower transmittance factor than calcium carbonate pigments. The differences between the various kaolin pigments were found to be very small, despite the large differences in their characteristics (cf. Table 5 and Figure 23). The same was true for the calcium carbonate pigments.



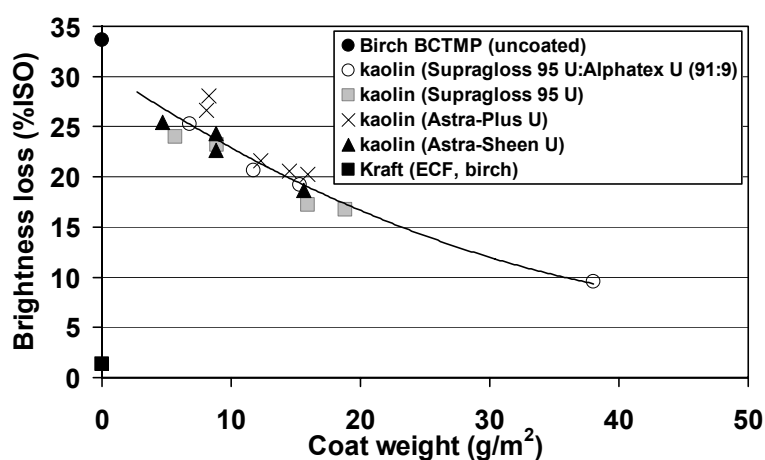
**Figure 24.** Transmittance factor,  $T_{dir}$ , in the 300–385 nm region of coating colours containing kaolin pigments. The measurements were conducted using the  $0^\circ/0^\circ$  geometry setup. For information of the pigments see Table 4.



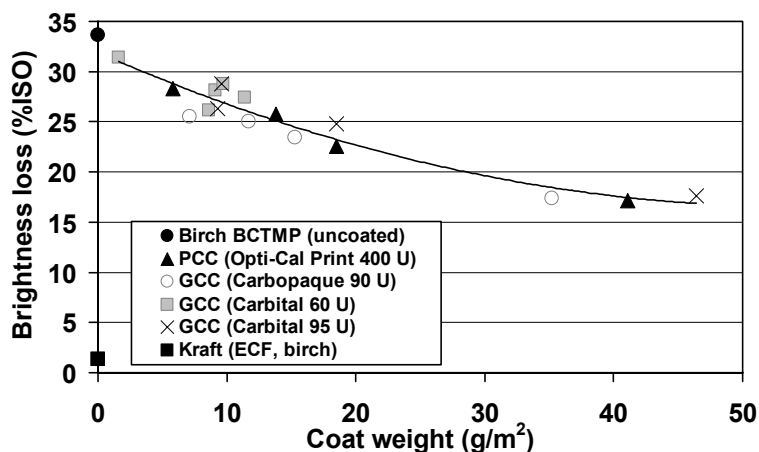
**Figure 25.** Transmittance factor,  $T_{dir}$ , in the 300–385 nm region of coating colours containing calcium carbonate pigments. The measurements were conducted using the  $0^\circ/0^\circ$  geometry setup. For information of the pigments see Table 5.

Figures 26 and 27 present the brightness reversion of hydrogen peroxide bleached birch CTMP as related to the transmittance factor,  $T_{dir}$ , of the coating colours using the newly developed method (see section 3.5 and Paper III). The change in ISO brightness after 24 hours of accelerated light-induced irradiation is shown in the figures. The overall brightness loss decreased with an increase in coat weight,

independently of the type of pigment used. As anticipated from the extent of transmittance, kaolin pigments were found to be better at photo-stabilising the base paper than calcium carbonate pigments. As with the transmittance measurements (cf. Figures 24 and 25), differences within the kaolin and calcium carbonate pigments respectively, were small, amounting to only a few brightness units. At a coat weight of approximately 12 g/m<sup>2</sup>, the base paper lost roughly five units more in brightness when coated with calcium carbonate pigments than it did when coated with kaolin pigments.



**Figure 26.** Brightness loss after accelerated light-induced ageing for 24 hours of uncoated and kaolin coated hydrogen peroxide bleached birch CTMP. The brightness loss is the brightness loss of the base paper (cf. Paper IV). The ageing characteristic of uncoated hydrogen peroxide bleached birch CTMP and ECF-bleached birch kraft pulp are given as a references. For information of the pigments see Table 4.

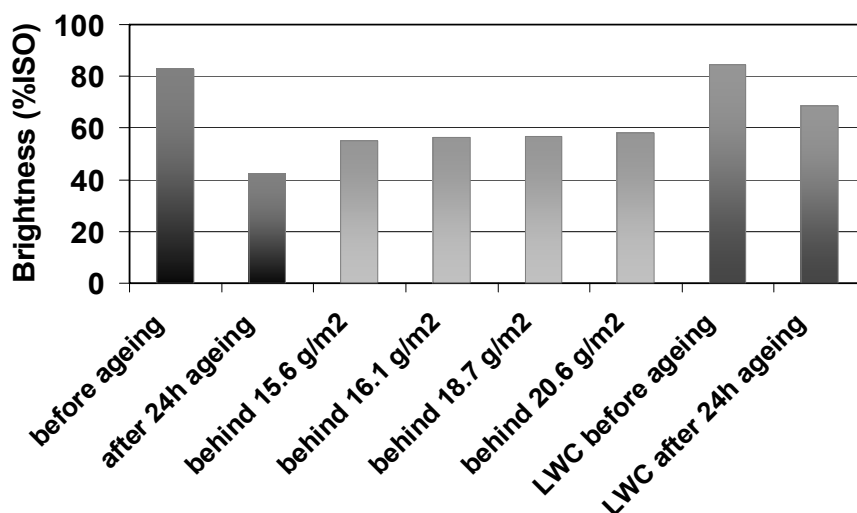


**Figure 27.** Brightness loss after accelerated light-induced ageing for 24 hours of uncoated and calcium carbonate coated hydrogen peroxide bleached birch CTMP. The brightness loss is the brightness loss of the base paper (cf. Paper IV). The ageing characteristic of uncoated hydrogen peroxide bleached birch CTMP and ECF-bleached birch kraft pulp are given as a references. For information of the pigments see Table 5.

The brightness loss in Figures 26 and 27 was calculated from measurements on the base paper, with no coated quartz glass plate in front of the paper (see description of method in Paper III and section 3.5). In reality, the coating layer itself will contribute to the optical properties of a paper, since it can conceal the colour formed through the light-induced brightness reversion at least to some extent. The concealing ability of the coating layers depends on the coat weight and the formulation of the coating colour.

To investigate the concealing impact of a coating layer, the brightness of a hydrogen peroxide bleached birch CTMP base paper was measured before and after 24 hours of accelerated light-induced ageing. Four quartz glass plates were coated with a coating colour containing Supragloss 95 U (kaolin), and the base paper was measured again with the quartz glass plates (one at a time) in front. The coating layer was facing the base paper during the measurements. The brightness reversion decreased by ~30% when the base paper was measured behind a coating layer with a coat weight of 15.6 g/m<sup>2</sup> (Figure 28). Increasing the coat weight (up to 20.6 g/m<sup>2</sup>) had only a marginal effect on the concealing ability of the coating layer. The ageing characteristic of a commercial light weight coated (LWC) paper was included for comparison. The brightness of the LWC paper was found to be more stable than that of the base paper, possibly in part because the base paper used in this investigation contained 100% mechanical pulp, whereas the LWC base paper contained only about 70% mechanical pulp. The LWC coating colour also

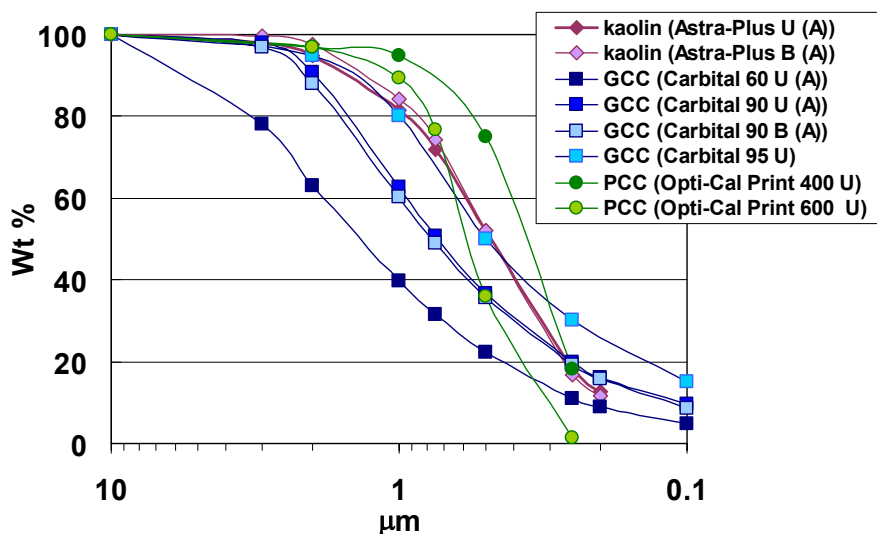
contained some FWA that may have increased the photo-stability of the LWC base paper (Bourgoing, Robert 1997; Bourgoing et al. 2001; Ragauskas et al. 2001).



**Figure 28.** Brightness of the hydrogen peroxide bleached birch CTMP base paper before and after 24 hours of accelerated light-induced ageing and the reverted brightness of the same paper measured behind quartz glass plates coated with the kaolin pigment Supragloss 95 U. The extent of photo-yellowing of a light weight coated (LWC) paper, aged under the same conditions, is included in the figure for comparison.

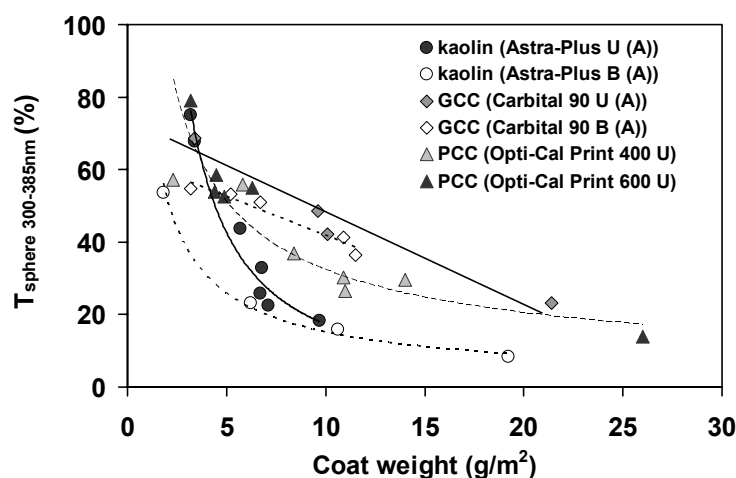
#### 4.3.2 More details about the influence of pigment type and bleaching of the pigment

To further distinguish the pigments, a new set of pigments were studied using the  $0^\circ/d$  geometry (see sections 3.4 and 4.2.1 for details) for measurement of the transmittance factor,  $T_{sphere}$ . The characteristics of the pigments can be found in Tables 4-5 and in Figure 29 below (for more detailed information see Paper V).



**Figure 29.** Particle size distribution of the kaolin and calcium carbonate pigments. For information of the pigments see Tables 4 and 5.

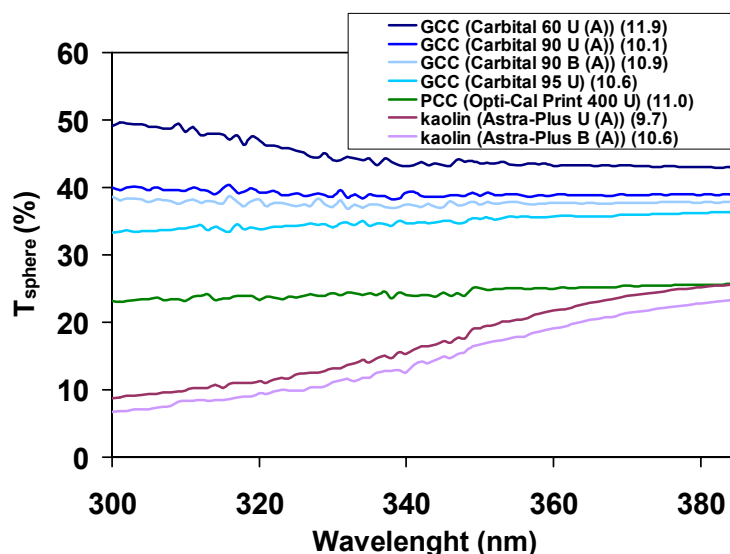
Figure 30 presents the transmittance factor,  $T_{sphere}$ , as a function of coat weight for a kaolin pigment (Astra-Plus) and a ground calcium carbonate (GCC) pigment (Carbital 90) before and after bleaching, and additionally unbleached precipitated calcium carbonate (PCC) pigments (Opti-Cal Print 400 and Opti-Cal Print 600). It is known from earlier work (Fossum et al. 1976; cf. Papers III and IV) that kaolin is more effective in retarding the light-induced yellowing than calcium carbonate pigments. This is supported by the results in Figures 30 and 31. At coat weights below about 10 g/m<sup>2</sup>, the bleached pigments were more effective in blocking the detrimental UV-radiation compared to the unbleached pigments. Bleaching caused a slight change in the psd of the pigments (cf. Tables 4-5 and Figure 29), leading to a somewhat modified structure in the coating layer, which will in turn have had an impact on the transmittance factor. Note the shape of the curves in Figure 30, an inflexion point in curves for kaolin occurs at ~10 g/m<sup>2</sup> and for PCC at ~8 g/m<sup>2</sup>. The inflexion point for GCC seems to take place at ~5 g/m<sup>2</sup> (cf. Figure 32).



**Figure 30.** The transmittance factor,  $T_{sphere}$ , in the 300-385 nm region of coating colours containing unbleached or bleached kaolin clay (Astra-Plus), GCC (Carbital 90) or PCC (Opti-Cal Print) pigments. The measurements were conducted using the 0°/d geometry setup. For information of the pigments see Tables 4 and 5.

Figure 31 shows the transmittance factor,  $T_{sphere}$ , as a function of wavelength between 300 and 385 nm for unbleached and bleached kaolin and calcium carbonate (GCC and PCC) pigments. In order to be able to compare the curves, the coat weight should preferably be of the same magnitude. The chosen coat weight (~11 g/m²) is a representative value for light weight coated (LWC) papers. The transmittance factor,  $T_{sphere}$ , of kaolin coatings decreased with decreasing wavelength, while the transmittance for calcium carbonate layers was more constant. Among the calcium carbonates, the GCC pigment, containing most fine particles (Carbital 95 U), and the PCC (Opti-Cal Print 400 U) gave a slightly decreased transmittance factor as the wavelength decreased. The coarsest GCC pigment (Carbital 60 U) showed an increase in transmittance factor,  $T_{sphere}$ , in the lower UV-region. Bleaching of the pigments, resulted in an overall decrease in transmittance factor for both kaolin and GCC pigments (cf. Figure 31).

Discolouration of lignin-containing pulps is mainly caused by wavelengths in the lower part of the UV-region (i.e., high-intensity radiation). Kaolin screens radiation better in this region compared to calcium carbonates which can be one reason to that kaolin is a better coating pigment to get photo-stability. PCC pigments seem to have a higher UV-screening potential compared to GCC pigments and are for that reason a better choice among the calcium carbonates for protecting wood-containing paper from photo-discolouration (cf. Figures 30 and 31).

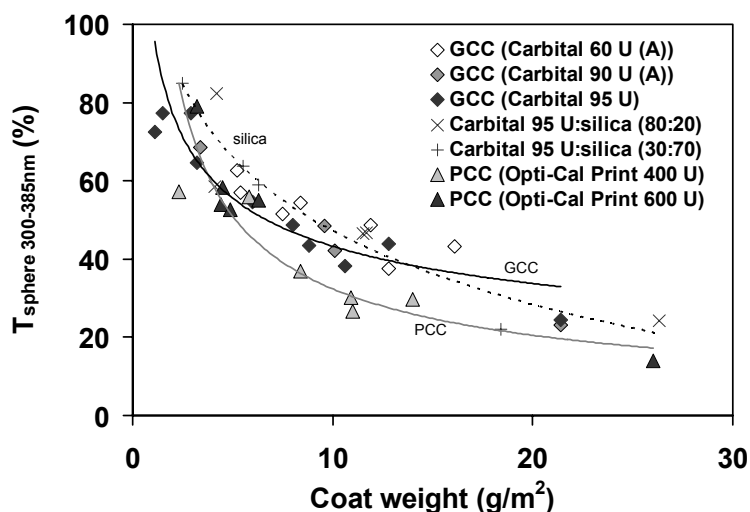


**Figure 31.** The transmittance factor,  $T_{sphere}$ , of coating colours containing unbleached or bleached kaolin clay (Astra-Plus) and calcium carbonate pigments (Carbital 60, 90, 95 and Opti-Cal Print 400). The coat weight in  $\text{g/m}^2$  is given in parentheses. The legends are shown in the same order as the curves. The measurements were conducted using the  $0^\circ/\text{d}$  geometry setup. For information of the pigments see Tables 4 and 5.

#### 4.3.3 Influence of particle size distribution

According to Figures 31 and 32, PCC pigments are better UV-blockers than GCC pigments. At higher coat weights, the disparity becomes more prominent. The PCCs, predominantly consist of pigment particles finer than  $2\ \mu\text{m}$ , and have very steep particle size distributions (cf. Table 5, Figure 29), while the GCCs mostly contain coarser, larger blocky particles

Among the GCCs, the transmittance factor was slightly lowered for the pigment consisting of smaller particles (cf. Figures 31). To achieve a low transmittance in the UV-region, it seems that a steep particle size distribution is favoured. This is in accordance with the fact that a steep particle size distribution gives higher porosity and consequently can enhance the light scattering (Bown 1997). Exchanging some of the GCC (Carbital 95 U) for silica particles produced a further slight decrease in transmittance factor at coat weights above  $15\ \text{g/m}^2$ , and a small increase in transmittance factor at coat weights below  $15\ \text{g/m}^2$ , compared to GCC (Carbital 95 U). The reason might be that the silica particles, which are very small particles (mean particle size;  $35\ \text{nm}$ ) fill up the void structure in the coating layer, and this will at a certain level decrease the light scattering.

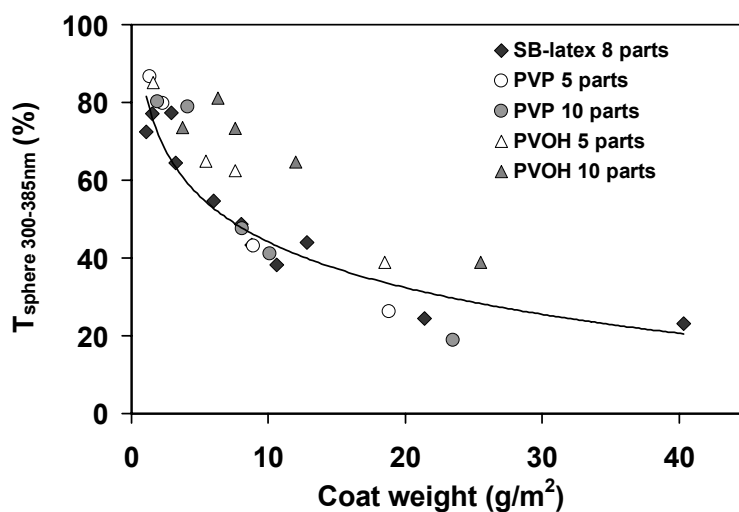


**Figure 32.** The transmittance factor,  $T_{sphere}$ , in the 300-385 nm region of coating colours containing calcium carbonate and silica pigments. The measurements were conducted using the  $0^\circ/d$  geometry setup. For information of the pigments see Table 4.

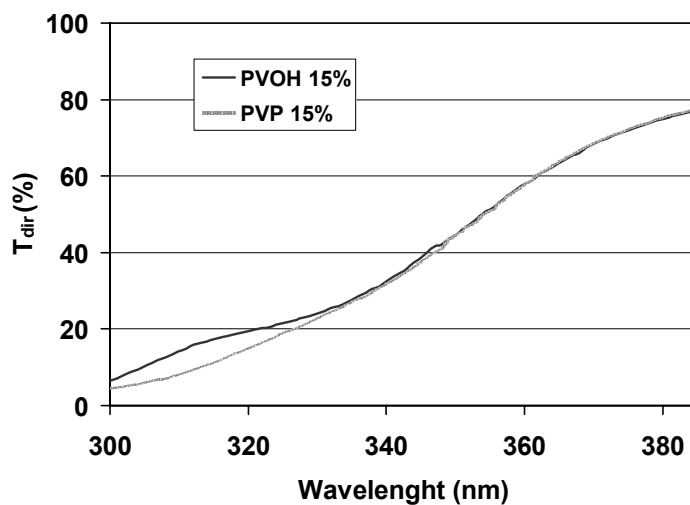
#### 4.3.4 Influence of binders

Binders are a necessary component in the coating colour and will impact the transmittance characteristics. The standard recipe used in this investigation contained 8 parts of a styrene butadiene latex (SB-latex). The styrene butadiene latex was exchanged for five or ten parts of PVP (polyvinylpyrrolidone) or PVOH (polyvinyl alcohol). PVOH shows an increase in  $T_{sphere}$  when increasing the amount of PVOH in the coating colour, and has an overall larger  $T_{sphere}$  compared to styrene butadiene latex, Figure 33. PVP did not seem to have any influence on the  $T_{sphere}$  as both five and ten parts of the PVP produced about the same outcome as SB-latex.

The transmittance of PVOH was higher below  $\sim 330$  nm compared to the transmittance of PVP (cf. Figure 34). Furthermore, the absorbance of PVOH was lower than that of PVP in the entire UV-region (results not shown here). This might be one explanation for the higher transmittance factor of coating colours containing PVOH as binder (see Figure 33). Another explanation could be the influence that binders have on the structure (e.g., porosity) of the coating layer.



**Figure 33.** The transmittance factor,  $T_{sphere}$ , in the 300-385 nm region of coating colours containing GCC pigment (Carbital 95 U) and various types of binders. The measurements were conducted using the  $0^\circ/d$  geometry setup.

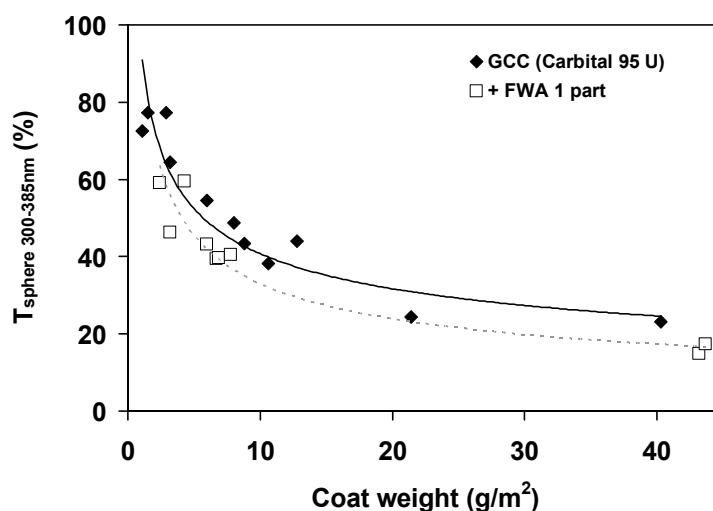


**Figure 34.** The transmittance factor,  $T_{dir}$ , of polyvinyl alcohol (PVOH) and polyvinylpyrrolidone (PVP). The transmittance factor was determined for water solutions containing 15% (as active component) PVOH or PVP. The measurements were conducted using the  $0^\circ/0^\circ$  geometry setup.

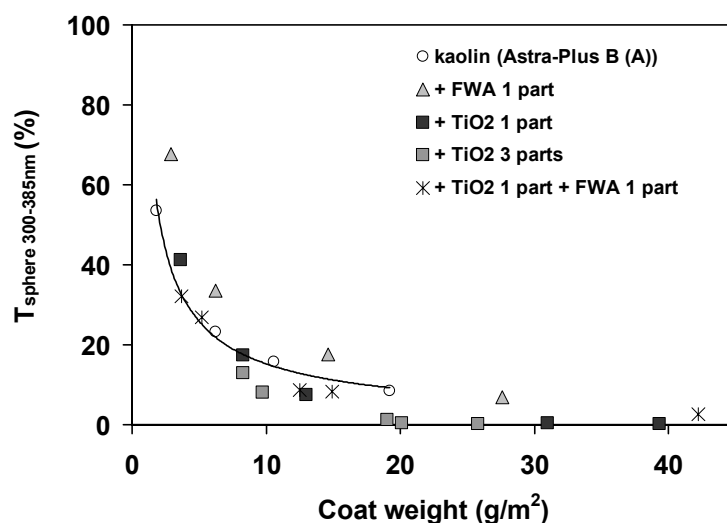
#### 4.3.5 Influence of UV-absorbing additives

Adding one part of a fluorescent whitening agent (FWA) to the standard coating recipe containing GCC pigments (Carbital 95 U) produced an overall decrease in

transmittance factor in the UV-region as expected, since the FWA has an absorption in this wavelength region (Figure 35). However, addition of FWA did not result in any improvement when kaolin (Astra-Plus B) was used as pigment; as a matter of fact, it even increased the transmittance factor (Figure 36, cf. Figure 21). The cause of this observation is not fully understood, but the  $T_{sphere}$  of the GCC coating formulation was much higher (cf. Figure 35) and this might have influenced the final outcome.



**Figure 35.** The transmittance factor,  $T_{sphere}$ , in the 300-385 nm region of coating colours containing GCC pigment (Carbital 95 U) and fluorescent whitening agent (FWA). The measurements were conducted using the 0°/d geometry setup. For information of the pigment see Table 5.



**Figure 36.** The transmittance factor,  $T_{sphere}$ , in the 300-385 nm region when combining kaolin pigment (Astra-Plus B) with different additives. The measurements were conducted using the 0°/d geometry setup. For information of the pigment see Table 4.

The light scattering ability of a coated paper increase with increasing difference in refractive indexes at interfaces between the materials in the paper, e.g. pigment-cellulose, pigment-air, pigment-binder etc. The only commonly used pigment with a refractive index significantly greater than that of cellulose (1.53) or water (1.33) is titanium dioxide ( $\text{TiO}_2$ ), which has a refractive index of 2.70 (Eklund, Lindström 1991). In addition to a high light scattering ability, titanium dioxide also has high absorption of radiation in the UV-region (Bown 1997). Titanium dioxide was therefore combined with the best pigment (kaolin) and binder (SB-latex) (Figure 36). As previously mentioned in section 4.2.3, a small addition of  $\text{TiO}_2$  lowered the transmittance. At higher coat weights (above 20 g/m²) the  $T_{sphere}$  turned out to be extremely low, even close to zero. However, at coat weights below ~10 g/m², the titanium dioxide showed little or no improvement at the addition levels used in this work (1 or 3 parts  $\text{TiO}_2$ ). Obviously, the distance between the  $\text{TiO}_2$  particles in the sheet structure must not be too long to get an improved UV-screening effect. However, at higher coat weights the addition of  $\text{TiO}_2$  had an evident effect. At coat weights common to a double coated paper, i.e. close to 20 g/m², the transmission of UV-radiation was close to zero, when 3 parts of  $\text{TiO}_2$  was added to the best coating recipe that has been tested in this thesis. This shows that it is possible to fully protect a double coated base paper from harmful UV-radiation. A prerequisite to reach so far is that the coating layer has an even coat weight.

## 5. SUMMARY

The main goal of this work was to find the prerequisite of increasing the usage of mechanical and chemimechanical pulps in high-quality paper grades that normally are essential wood free such as fine paper grades, and in wood containing magazine grades such as LWC and SC at maintained or reduced light-induced discolouration. The results show that even small amounts of hydrogen peroxide bleached hardwood CTMP (from birch) causes severe discolouration upon irradiation. Moreover, all of the investigated mechanical and chemimechanical pulps suffered from light-induced discolouration and lost brightness no matter how they were produced. The main factor that determines the extent of discolouration is the lignin content of the pulps and hence, hardwood high-yield pulps (especially aspen pulps) are more photo-stable than softwood pulps.

Coating of the wood-containing paper is an efficient way to get an adequate photo-stability. The UV-screening properties of the coating layer were therefore determined and optimized by selecting proper pigments, binders and UV-absorbing additives. To be able to do this, a unique method was developed that made it possible to determine the transmission of UV-radiation through thin coating layers with well defined coat weights. The most important component of the coating colour for the UV-screening properties seems to be the pigment type. Kaolin, which has a platy flake-like shape, was shown to have good UV-filtering capacity. Bleaching of the kaolin further enhanced the UV-blocking properties. A narrow pigment size distribution was also shown to be important, although not to the same extent as the pigment type. At coat weights corresponding to that of a double coating, i.e. close to 20 g/m<sup>2</sup>, the UV-transmission is close to zero, when 3 parts of TiO<sub>2</sub> was added to the best coating formulation, containing bleached kaolin pigments. This shows that it is possible to more or less fully protect a double coated base paper from harmful UV-radiation, when the coating layer have an optimum composition for that purpose. A prerequisite to reach so far is that the coating layer has an even coat weight.

## 6. CONCLUSIONS

When evaluating the brightness reversion of commercial softwood and hardwood high-yield pulps, accelerated light-induced ageing overestimated the discolouration tendencies of hardwood pulps, especially in the case of aspen high-yield pulps. Accelerated light-induced ageing could, however, predict the extent of discolouration of softwood pulps, regardless of the pulping or bleaching method used. One unexpected finding was that when using ambient ageing, over longer periods of time, pulps made of birch (with the exception of birch alkaline peroxide mechanical pulp) approached the softwoods in brightness reversion. Evaluation of the ageing characteristics using the CIELAB colour system showed that accelerated ageing conditions tended to mainly increase the  $b^*$  value and decrease the  $L^*$  value (i.e. yellow the pulp), whereas long-term ambient ageing also increased the  $a^*$  value which making the pulp more reddish. Ambient light-induced ageing caused a continuous discolouration over time, while accelerated light-induced ageing was characterised by a rapid initial discolouration followed by a slower, less detrimental secondary phase. Softwood pulps displayed a greater change in the  $a^*$  coordinate than hardwood pulps, which showed a less linear increase with time. Papers produced from alkaline peroxide mechanical pulps exhibited the least change in colour. There seemed to be a strong correlation between lignin content of the pulps and the extent of discolouration.

Coating layers were shown to have some ability both to hinder parts of the UV-radiation from reaching the base paper and to conceal some of the colour formed during light-induced brightness reversion, depending on coating colour composition and applied coat weight. The results obtained using a newly developed method to determine the transmission of UV-radiation through coating layers were found to be highly reliable even for low coat weights ( $<10 \text{ g/m}^2$ ). Moreover, the transmittance in the UV-region of a coating layer and the layer's ability to protect hardwood (birch) chemimechanical pulp (CTMP) against discolouration were shown to be strongly correlated.

Coating colours containing kaolin pigments had a lower transmittance in the UV-region (300–385 nm) than coating colours containing calcium carbonate pigments. Using a hydrogen peroxide bleached birch CTMP as the base paper, kaolin pigments were consequently found to have better photo-stabilising properties than calcium carbonate pigments. Of the calcium carbonates, precipitated calcium carbonates (PCCs) were better than ground calcium carbonates (GCCs) in screening UV-radiation, and the difference is greater at higher coat weights. Bleaching of the pigments resulted in an overall decrease in transmittance for both kaolin and GCC pigments, especially at low coat weights. The particle size distribution should preferably be narrow in order to reduce the UV-radiation. When the binder styrene butadiene latex was exchanged for polyvinylpyrrolidone, there was no difference in transmittance, but when using

polyvinyl alcohol as binder, the transmittance increased. Adding a fluorescent whitening agent to the coating colour decreased the transmittance factor when the pigment used was GCC, and increased it when the pigment used was kaolin. Combining the best pigment (kaolin, Astra-plus B) and the best binder (styrene butadiene latex) with titanium dioxide (3 parts), the transmittance in the UV-region could be reduced by about 90% at a coat weight of  $\sim 10 \text{ g/m}^2$ . At a coat weight close to  $20 \text{ g/m}^2$  the transmittance was close to zero.

## **7. FUTURE WORK**

This work has provided knowledge about how to prevent high-yield pulps from being discoloured by light. To validate the results obtained from accelerated light-induced ageing, it would be desirable to perform ambient light-induced ageing of the same samples. The research of suitable pigments can be extended to include custom-made PCCs with different shapes and sizes, and different combinations of pigments. Other types of pigments not included in this work, for example, zinc oxide, would also be interesting to study. The influence of fluorescent whitening agents need to be investigated in more detail, since only one type of FWA was tested in this work. UV-absorbers are not only used in the paper industry, but can found in paint, plastic, cosmetic, textile etc. These UV-absorbers are of interest as well, and should therefore be investigated. Moreover, this new method can be used to optimise the coating layer, for example by studying the optical properties, such as light scattering coefficient,  $s$ . In addition, the method can achieve detailed information of the transmittance in different wave length regions, which potentially can lead to new understandings regarding the mechanism of light-induced discolouration.

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