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The UV-screening properties of coating layers: The influence of pigments, binders and additives

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KEYWORDS: UV-screening, Photo-stability, Coating, Pigments, Kaolin, Calcium carbonate, GCC, PCC, Binders, Titanium dioxide, FWA, PVOH, PVP

SUMMARY: The ability of coating colours to obstruct ultra-violet (UV) radiation in the 300-385 nm region was examined with the aim of finding the best photo-stabilising formulation to inhibit discoloration of high-yield pulps. The influence of pigment type, bleaching of the pigments, pigment size, pigment size distribution, type of binder and addition of UV-absorbing compounds were examined using a newly developed method for studying the reflectance and transmittance properties of thin coating layers.

The pigment type and coat weight was found to be the most important factors for reducing the transmittance of UV-radiation. Kaolin clays were more effective than calcium carbonate pigments and are therefore a better coating pigment for photo-stability reasons. Bleaching of the pigments, resulted in an overall minor decrease in transmittance for both kaolin and ground calcium carbonate (GCC) pigments, especially at low coat weights. Bleaching of the pigments changed the particle size distribution somewhat, which probably alters the structure in the coating layer. Precipitated calcium carbonate (PCC) pigments have a higher UV-screening potential compared to GCC pigments and should therefore be a better choice among the calcium carbonates. It was further concluded that a narrow pigment size distribution was beneficial for reducing the amount of transmitted UV-radiation that reaches the base paper. Styrene butadiene latex and polyvinylpyrrolidone were better in reducing the transmittance in the UV-region than polyvinyl alcohol.

Adding a fluorescent whitening agent to a coating colour decreased the transmittance in the UV-region when the pigment was of the GCC type, and increased the transmittance when kaolin pigment was used. Addition of titanium dioxide (3 parts) to a coating colour containing kaolin pigment blocked about 90% of the UV-radiation at a coat weight of 10 g/m², which is a common coat weight for a single coated paper. Another possibility is to double coat to increase the coat weight, which turns the transmittance factor closed to zero.

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Mechanical and chemimechanical pulps can be produced with lower capital costs and have less impact on the environment than chemical pulps. These pulps also have other advantages such as high yield and bulk, good printing properties, high opacity and light scattering ability, all of

which make it possible to lower the basis weight of the produced paper or paperboard. The rapid brightness reversion (discoloration) that occurs upon exposure to daylight or indoor illumination is, however, a serious limitation hindering mechanical or chemimechanical pulps to be used in high-quality long-life paper products. When the paper is subjected to sunlight or indoor illumination containing UV-radiation, chromophores absorbing light in the blue-green region are formed, and it is generally accepted that it is lignin constituents that are responsible for this discoloration (Gratzl 1985; Heitner 1993; Leary 1994; Davidson 1996; Forsskåhl 2000; Lanzalunga, Bietti 2000).

Coating of paper has the potential to retard the discoloration and is most likely necessary for photo-stability reasons if pulps containing lignin are to be used as the main fibre-furnishing component in long-life and high-value products. The amount and 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). Kaolin clay has been reported to be somewhat more effective in retarding the accelerated light-induced yellowing compared to a coating layer containing calcium carbonate pigments (Fossum et al. 1976; Reinhardt, Arneberg 1988; Fjellström et al. 2007a; Fjellström et al. 2007b). Luo and Götsching (1991) reported that kaolin was somewhat more effective in retarding the photo-yellowing of a base paper intended for light weight coated paper grades than a brighter calcium carbonate pigment. They also found that when combining kaolin and calcium carbonate pigments, the performance where improved to some extent. On the other hand, Krogerus and Forsskåhl (1995) found calcium carbonate to be superior to other pigments in light-induced ageing experiments.

Substitution of some of the kaolin with TiO₂ was shown to improve the photo-stability of paper containing thermomechanical pulp (TMP) (Fossum et al. 1976; Yuan et al. 2003). According to Johnson (1991), coating a hydrogen-peroxide-bleached chemithermomechanical pulp (CTMP) with a coat weight of about 4g/m² of clay gives 20% improvement in Δk_{457nm} when the CTMP is subjected to accelerated (sunlamps) light-induced yellowing. This improvement could be increased to 60% by using kaolin:TiO₂ in the ratio 80:20. Yuan et al. (2006) reported that a coated (calcium carbonate, 80pph/delaminated clay, 20pph, 20 g/m²) kraft sheet with a 15% substitution of bleached birch CTMP gave the same brightness stability as a 100% kraft sheet coated at 4 g/m². The evaluation was made using both accelerated (fluorescent

lamps) and natural long-term light-induced ageing.

The particle size distribution of the pigment is known to have an effect on the light scattering ability (Lindblad et al. 1989; Bown 1997). A steep particle size distribution gives higher porosity and has the advantage of creating void space in the dried structures and hence could enhance the light scattering. If maximum light scattering is desired in a certain wavelength region (e.g., the UV-region) the pore diameter should be of a magnitude such that the ratio of pore diameter to wavelength is approximately 0.5 and preferably all the pores should be of the same size (Lindblad et al. 1989). A monodisperse pigment particle system of this type could offer a high UV-scattering ability that could improve the photo-stability considerably. The influence of particle size and distribution of commercial coating pigments on the UV-screening properties of coating layers are therefore important to examine.

The binders and thickeners in the coating colour also effect the brightness stability of a coated paper since they may turn yellow themselves upon light exposure. For example, polyester-polynitrile is more photo-stable than butadiene-styrene (Reinhardt, Arneberg 1988; Luo, Götsching 1991). In addition, additives like fluorescent whitening agents (FWAs) and 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). The carriers inhibit the photo-induced degradation of FWA and some of the carriers have also been used to photo-stabilise lignin-containing pulps.

PEG with different molecular weights and different end groups have been used to prevent light-induced yellowing, but relatively large amounts is needed (Minemura 1978; Janson, Forsskåhl 1989; Ragauskas et al. 2001). PVP has been found to in addition to inhibit the photo-yellowing, also increase the initial brightness (Rättö et al. 1993; Hortling et al. 1993). Polytetrahydrofurans (PTHF) is another polymer that has been used to reduce the brightness reversion (Janson, Forsskål 1996).

The use of FWAs 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 was found to retard brightness reversion by 25% compared to untreated paper. Furthermore, a reduction in chromophore formation with up to 80%, after 5 hours of UV irradiation was shown when FWA was sprayed onto unbleached TMP (Bourgoing, Robert 1997; Bourgoing et al. 2001).

Another way of inhibiting light-induced yellowing is to use UV-absorbers (UVA) in the pulp or on the paper surface to block out damaging UV-radiation. Derivates of benzophenone has been found to have a positive effect on brightness reversion (Kringstad 1969; Gellerstedt et al. 1983; Fournier de Violet et al. 1990; Paulsson, Ragauskas 1998b; Argyropoulos et al. 2000; Peng, Argyropoulos 2000; Weir, Miller 2000). Applying a combination of UVA, radical scavenger (RS) and TiO₂ on alkaline peroxide mechanical pulp (55% spruce and 45% aspen) resulted in higher initial brightness and better brightness stability

without effecting the rheology of the coating colour (Yuan et al. 2004). El-Sadi et al. (2002) reported that the yellowing inhibition is most sensitive to total inhibitor charge, and strongly depends on the RS/UVA ratio.

The present paper examines the ability of coating colours to obstruct ultra-violet (UV) radiation in the 300–385 nm region with the aim of finding the best photo-stabilising formulation to inhibit discoloration of high-yield pulps. The influence of pigment type, bleaching of the pigments, pigment size, pigment size distribution, type of binder and addition of UV-absorbing compounds were examined.

Materials and Methods

Pigment, binders and additives

The standard coating formulation consisted of a pigment (100 parts), styrene butadiene (SB) latex (8 parts) and carboxymethylcellulose, CMC, (0.5 parts). The pH of the coating colour was adjusted to 8.5 with 5M NaOH. The different pigments and binders used in the study are described below. More detailed information about the kaolin clays and calcium carbonate pigments used can be found in *Table 1*.

The pigments used were kaolin (Astra-Plus unbleached/bleached), ground calcium carbonates (GCCs; Carbital 60 unbleached, Carbital 90 unbleached/bleached, Carbital 95 unbleached) precipitated calcium carbonates (PCCs; Opti-Cal Print 400 unbleached, Opti-Cal Print 600 unbleached) obtained from Imerys, UK and Silica (Bindzil 50/80, density 1.397 g/cm³, specific surface 90 m²/g, mean particle size 35 nm) obtained from Eka Chemicals, Sweden. Bleaching of the kaolin pigment, Astra-Plus, was performed using sodium dithionite and the calcium carbonate, Carbital 90, was bleached using sodium formamidine sulphinate. The binders used were a SB-latex (DL920, DOW, Sweden), CMC (FF10, Noviant, the Netherlands), PVP (Lumiten P-PR 8450, BASF, Germany) and PVOH (Mowiol 30-92, Kuraray Specialities Europe GMBH, Germany). The molecular weights of the binders were 65000 g/mol (CMC), 10000 g/mol (PVP) and 175000 g/mol (PVOH).

Fluorescent whitening agent, FWA, (Tinopal UP, diaminostilbene disulphonic acid type, Ciba Specialty Chemicals, Switzerland) and titanium dioxide (TiO₂, rutile, Kronos 2063S, Kronos-Titan, GmbH, Germany) were added to the coating colour as UV-screening additives.

Coating procedure

Quartz glass plates were coated in a laboratory coater using a glass rod to spread the coating colour. To obtain various coat weights the speed of the glass rod was varied. The coating layer was dried at room temperature before UV-VIS spectroscopic analysis. The basis weight (g/m²) of the coating layer was determined as previously reported in Fjellström et al. (2007a).

UV-VIS diffuse reflectance spectroscopy

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 presented spectra for each sampling point are mean values from at least 3 measurements. 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. The transmittance of the uncoated quartz glass plates determined in this way was in the range of 90–93%. 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 or reflectance factors. For detailed information of the UV-VIS diffuse reflectance spectroscopy measurements, see Fjellström et al. (2007a).

Results and Discussion

Coating of wood-containing papers is one option to improve photo-stability and it is therefore important to study the effect of pigment, binders and additives to optimise the coating colour formulation. There are discrepancies in the literature regarding the effect of these components (see introduction). A novel method for studying the reflectance and transmittance of thin coating layers has been used to determine the UV-screening properties of the consisting components. The methodology has been thoroughly described in Fjellström et al. (2007a), for instance the significance of transmittance measurements at low coat weights and the possibility to determine light scattering and light absorption characteristics of coating layers.

Characterisation of the pigments used

Table 1 shows some characteristic properties (brightness, particle size and distribution and surface area) of the kaolin and calcium carbonate pigments used in this work. The kaolin clay pigments are platy flake like particles. Opti-Cal Print 400/600 which are precipitated calcium carbonates, PCCs, consists of many small pigment particles that are aggregated into larger aggregates. The other calcium carbonates are ground marbles, (GCCs, ground calcium carbonates), that are blocky sphere like pigments. Kaolin clays generally have a lower brightness (6-10 brightness units) than the calcium carbonates, (cf. Table 1) mainly due to their higher light absorption ability (Bown 1997). As can be seen in Fig 1, the GCCs have a more broad particle size distribution (psd) compared the other pigments. Carbital 60 consists of bigger particles than Carbital 90, which in turn consists of slightly bigger particles than Carbital 95. The pigment size of the kaolin pigments (Astra-Plus) is of the same magnitude as Carbital 95, but has a somewhat narrower psd (cf. Fig 1). The PCCs (Opti-Cal Print) are monodis-

Table 1. Data for the kaolin and calcium carbonate (GCC, PCC) pigments used in this work as obtained from Imerys.

Pigment	Bleached / Unbleached B / U	Wt%					D50, μm^1	Surface area (m^2/g)	Brightness (% ISO)
		<2 μm	<1 μm	<0.5 μm	<0.25 μm	<0.10 μm			
Kaolin clays									
Astra-Plus	U	95	81	52	18	n.a. ²⁾	0.45	11.6	86.2
Astra-Plus	B	98	84	52	17	n.a. ²⁾	0.45	12.2	88.2
GCC									
Carbital 60	U	63	40	22	11	5	1.5	7.6	95.3
Carbital 90	U	91	63	37	20	10	0.72	12.0	94.7
Carbital 90	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
PCC									
Opti-Cal Print 400	U	97	95	75	16	n.a. ²⁾	0.40	9.2	96.0
Opti-Cal Print 600	U	97	90	36	2	n.a. ²⁾	0.57	7.4	96.6

¹⁾ Median particle size

²⁾ Not available

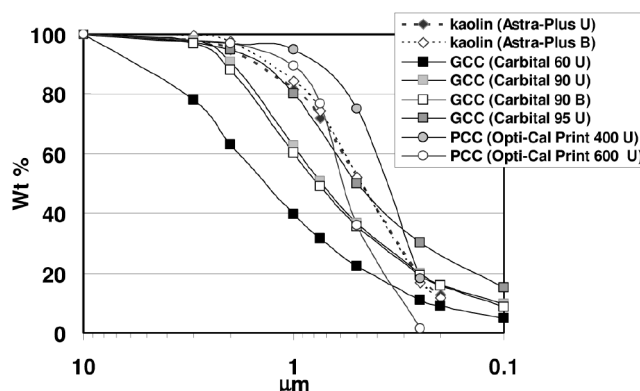


Fig 1. Particle size distribution of the kaolin and calcium carbonate pigments (Data from Imerys. Sedimentation technique).

perse pigment particle systems and therefore have very steep particle size distributions. Moreover, the PCC particles are rather small. Bleaching of the kaolin pigment was performed using sodium dithionite, and the calcium carbonate was bleached using sodium formamidine sulphinate.

Transmittance in the UV-region (300–385 nm)

Figs 2-8 shows the transmittance factor in the UV-region (300–385 nm) of coating colours containing kaolin or calcium carbonate pigments and the transmittance factor of polyvinylpyrrolidone (PVP) and polyvinyl alcohol (PVOH) binders. The UV-region 300–385 nm was chosen since the transition from photo-yellowing to photo-bleaching of lignocellulosic materials occurs at wavelengths around 385 nm (cf. e.g. Nolan et al. 1945; Leary 1967; Andtbacka et al. 1989; Mailly et al. 1996). The transition is, however, not fixed to a certain wavelength but depends on several things such as e.g., wood raw material and pulping method used (cf. Heitner 1993).

Pigment type

Fig 2 shows the transmittance factor, T_F , as a function of coat weight for a kaolin clay pigment (Astra-Plus) and a ground calcium carbonate pigment (Carbital 90) before and after bleaching. As known from earlier work (Fossum et al. 1976; Fjellström et al. 2007a; Fjellström et al. 2007b) kaolin is more effective in retarding the light-induced yellowing than calcium carbonate pigments. This

is supported by the results in *Figs 2 and 3*. At coat weights below about 10 g/m², the bleached kaolin pigments are more effective in blocking the detrimental UV-radiation compared to the unbleached kaolin pigments. During bleaching of the pigments, their psd is slightly changed (cf. *Table 1*). This probably leads to a somewhat changed structure in the coating layer, which will have an impact on the transmittance factor. The shape of the curves in *Fig 2* indicates that at low coat weights the transmittance factor of the different pigments are about the same, and very sensitive to small changes in coat weight. *Fig 3* shows the transmittance factor as a function of wavelength in the 300-385 nm region 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 is close to 11 g/m² which is a representative value for light weight coated (LWC) papers. It is evident from *Fig 3* that the kaolin pigments behave dissimilar from the calcium carbonate pigments. The transmittance factor of kaolin decreases with decreasing wavelength, while the calcium carbonates display a more independent manner. The GCC pigment containing most fine particles (Carbital 95 U) and the PCC pigment (Astra-Plus U) slightly decreases in transmittance factor as the wavelength decreases. The coarsest GCC (Carbital 60 U) displays an increase in transmittance factor in the lower UV-region. Bleaching of the pigments indicates an overall minor decrease in transmittance factor for kaolin and GCC pigments, something that is supported by the results presented in *Fig 2*.

The strongest discoloration of lignin-containing pulps is caused by wavelengths in the lower part of the UV-region (i.e., high intensity radiation). Kaolin clay screens radiation better in this region compared to calcium carbonates and is therefore a better coating pigment for photo-stability reasons. PCC pigments seem to have a higher UV-screening potential compared to GCC pigments and should therefore be a better choice among the calcium carbonates for protecting wood-containing paper from photo-discoloration (cf. *Figs 2 and 3*).

Particle size distribution

Of the investigated pigments, PCC pigments are better UV-blockers than GCC pigments, see *Fig 3*. At higher coat weights, the disparity becomes more prominent. The PCCs consists predominantly of pigment particles finer than 2 μm, and have very steep particle size distributions (cf. *Table 1, Fig 1*). Among the GCCs, the transmittance factor, T_F , is slightly lowered when the pigment consists of smaller particles. From the transmittance factor, it seems that a steep particle size distribution is favoured for obtaining a low transmittance in the UV-region. 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 display a slight decrease in transmittance factor at coat weights above 15 g/m², and a small increase in transmittance factor at coat weights below 15 g/m², compared to GCC (Carbital 95 U), see *Fig 4*. The silica particles are

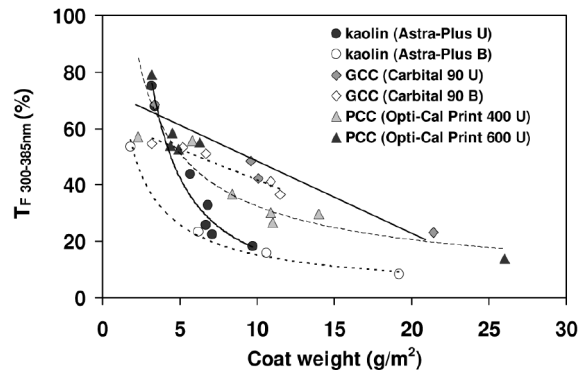


Fig 2. The transmittance factor, T_F , in the 300-385 nm region of coating colours containing unbleached or bleached kaolin clay (Astra-Plus), GCC (Carbital 90) or PCC (Opti-Cal Print) pigments. To illustrate the differences between the different types of pigments one curve is drawn for kaolin, GCC and PCC respectively. More information of the pigment can be found in *Table 1* and *Fig 1*.

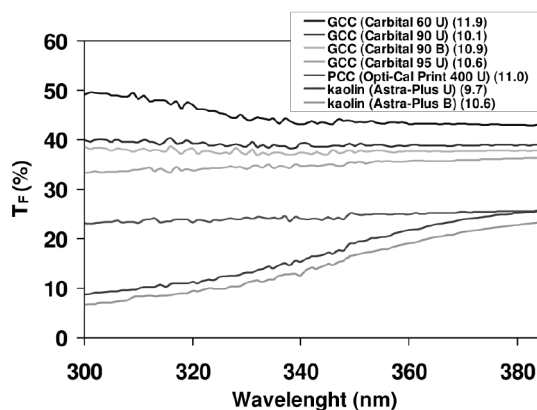


Fig 3. The transmittance factor, T_F , of coating colours containing unbleached or bleached kaolin clay (Astra-Plus) and calcium carbonate (Carbital 60, 90, 95 and Opti-Cal Print 400) pigments. The coat weight in g/m² is given in parenthesis. The legends are in the same order (top to bottom) as the curves in the figure. More information of the pigment can be found in *Table 1* and *Fig 1*.

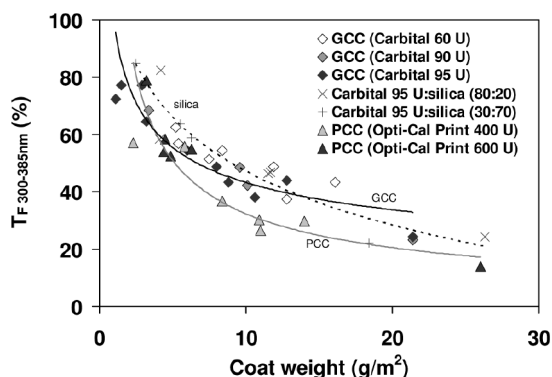


Fig 4. The transmittance factor, T_F , in the 300-385 nm region of coating colours containing calcium carbonate (GCC and PCC) and silica pigments. To illustrate the differences between the different types of pigments one curve is drawn for GCC, PCC and Carbital 95:silica, respectively.

very small particles (mean particle size 35 nm) and fill up the void structure in the coating layer, which will at a certain level decrease the light scattering ability.

Binders

Binders are necessary components in the coating colour and will impact the UV-screening properties, and are therefore important to investigate. The standard coating

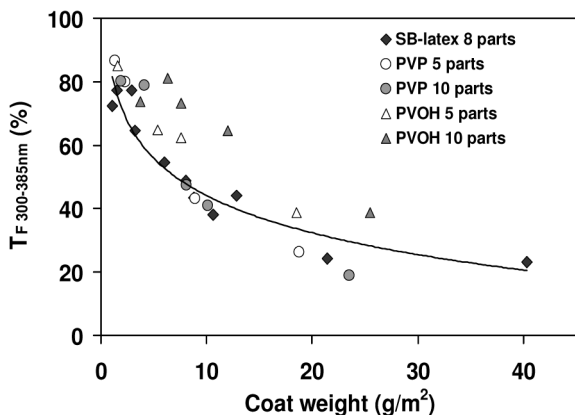


Fig 5. The transmittance factor, T_F , in the 300-385 nm region of coating colours containing a GCC pigment (Carbital 95 U, cf. Table 1) and various types of binders. The curve represents the standard coating formulation used in this investigation containing SB-latex.

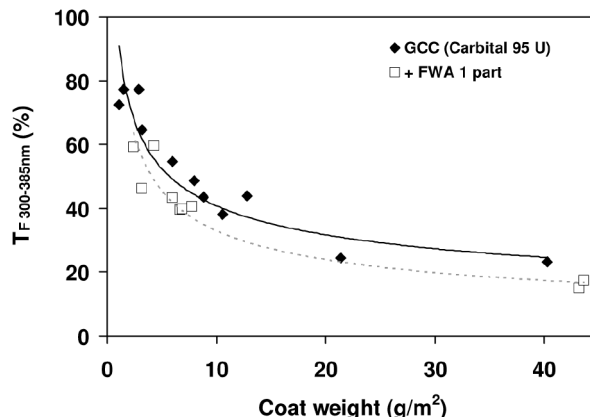


Fig 7. The transmittance factor, T_F , in the 300-385 nm region of coating colours containing GCC pigment (Carbital 95 U, cf. Table 1) and fluorescent whitening agent (FWA).

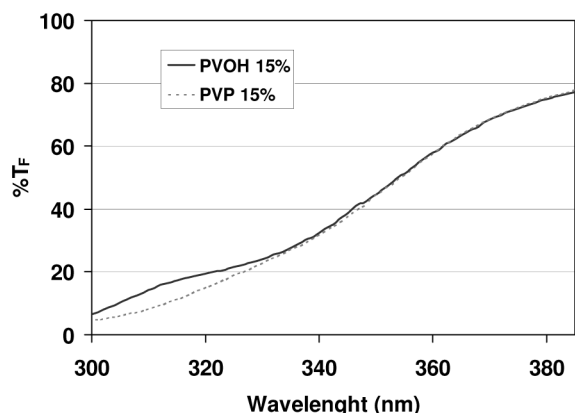


Fig 6. The transmittance factor, T_F , of polyvinyl alcohol (PVOH) and polyvinylpyrrolidone (PVP). The transmittance factor was determined for water solutions containing 15% (as active component) PVOH or PVP. The baseline correction was performed using water.

formulation used in this investigation contains 8 parts of styrene butadiene latex (SB-latex) and 0.5 parts of carboxymethylcellulose (CMC). It is known that SB-latex may slightly affect the brightness/whiteness upon light exposure, but the effect is of minor importance compared to the light-protecting properties of the coating layer (Reinhardt, Arneberg 1988; Luo, Göttching 1991). The styrene butadiene latex was exchanged for five or ten parts of PVP (polyvinylpyrrolidone) or PVOH (polyvinyl alcohol) and the influence on the transmittance factor can be found in Fig 5. Adding PVOH results in an overall larger T_F compared to SB-latex. PVP does not seem to have any influence on the T_F as both five and ten parts of the PVP in the coating colour provide the same outcome. The transmittance of PVOH is higher below ~ 330 nm compared to the transmittance of PVP, see Fig 6. Furthermore, the absorbance of PVOH is lower than that of PVP in the entire UV-region (results not shown here). This might be one explanation to the higher transmittance factor of coating colours containing PVOH as binder (cf. Fig 5). Another explanation could be the influence that binders have on the structure (e.g., porosity) of the coating layer.

UV-absorbing additives

Adding one part of a fluorescent whitening agent (FWA) to a coating formulation containing GCC pigments

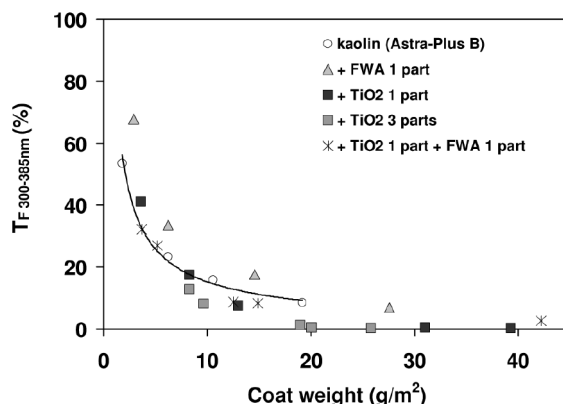


Fig 8. The transmittance factor, T_F , in the 300-385 nm region when combining kaolin pigment (Astra-Plus B, cf. Table 1) with the UV-absorbing additives fluorescent whitening agent (FWA) or titanium dioxide (TiO_2).

(Carbital 95 U) showed an overall decrease intransmittance factor in the UV-region as expected since the FWA has an absorption in this wavelength region (Fig 7). Addition of FWA did, however, 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 (cf. Fig 8). The cause of this observation is not fully understood, but the T_F of the GCC coating formulation was much higher (cf. Fig 7) and this might influence the end results. The UV-radiation passing the coating layer will be reduced when FWA is present, but the UV-radiation may also generate a fluorescence radiation that can be recorded by the detector, thus giving an increase in T_F .

The light scattering ability of a coated paper increases with increasing difference in refractive indexes at interfaces between the materials in the paper, e.g. pigment-cellulose, pigment-air, pigment-binder etc. Titanium dioxide (TiO_2 , rutile) is the only commonly used pigment with a refractive index (2.70) significantly greater than that of cellulose (1.53) or water (1.33) (cf. Lehtinen 2000; Pauler 2002). 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) (Fig 8). As expected on the basis of previous research (Fossum et al. 1976; Gellerstedt et al. 1983; Johnson 1989, 1991; Ghosh et al. 2002; Fjellström

et al. 2007a), a small addition of TiO₂ lowered the transmittance. At higher coat weights (above 20g/m²) the T_F turns out to be extremely low, even close to zero. However, at coat weights below ~10 g/m², the titanium dioxide shows little or now improvement for the addition levels used in this work (1 or 3 parts TiO₂).

Important factors for obtaining coating layers with a high UV-screening ability

To get a very low T_F and hence a quite photo-stable paper the main objective to focus on seems to be the pigment type. The platy flake-like shape of kaolin clays gives a good coverage capacity and the higher light absorption of these pigments make them the preferred pigment to use to obtain a paper that is as photo-stable as possible. Bleaching of kaolin reduces the transmittance factor somewhat at coat weights below approximately 10g/m², probably due to generating a steeper particle size distribution. A narrow pigment size distribution is important, although not to the same extent as the pigment type and coat weight.

A coating layer containing bleached kaolin (Astra-Plus B) pigments and 3 parts titanium dioxide obstructs ~90% of the destructive UV-radiation (in the 300-385 nm region) at a coat weight of 10 g/m² which is a common coat weight for a single coated paper (cf. Fig 8). The lower transmission in the UV-region of this coating layer is expected to increase the photo-stability of a coated paper, (calculated from the ISO brightness loss due to irradiation) with about 65% when compared to the yellowing characteristics of a uncoated base paper consisting of 100% mechanical or chemimechanical pulp (cf. Fjellström et al. 2007a; Fjellström et al. 2007b). The discoloration of a single coated wood-containing paper will thus still be extensive and other photo-stabilising measures are probably necessary for long-life paper products. Such treatments could include the addition of UV-absorbing organic (e.g., benzophenone and benzotriazole derivatives) or inorganic (e.g., zinc oxide) compounds to the coating layer. The methodology used in this work and described in Fjellström et al. (2007a,b) could be used to evaluate such treatments. Another possibility is to use double coating to increase the coat weight. A coating layer consisting of bleached kaolin pigments (19.2 g/m², simulating a double coating of 10 g/m² per layer) corresponds to a single coating layer (10 g/m²) of bleached kaolin pigments where 3 parts of titanium dioxide had been added, see Figs 9 and 10. Increasing the coat weight of the coating colour containing titanium dioxide (3 parts) to 19.0 g/m², resulted in a transmittance factor close to zero. 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.

Conclusions

Coating colours containing unbleached or bleached kaolin pigments have a lower transmittance factor, T_F , in the UV-region (300-385 nm) than coating colours containing calcium carbonate pigments. Of the calcium carbonates, precipitated calcium carbonates (PCCs) are

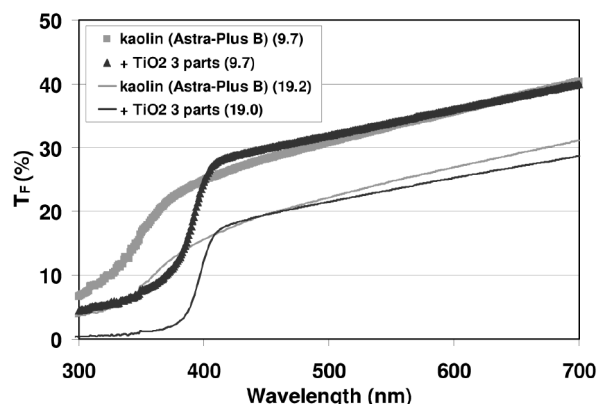


Fig 9. The transmittance factor, T_F (in the 300-700 nm region) of coating colours containing bleached kaolin clay (Astra-Plus B) and the UV-absorbing additive titanium dioxide (TiO₂). The coat weight in g/m² is given in parenthesis. More information of the pigment can be found in Table 1 and Fig 1.

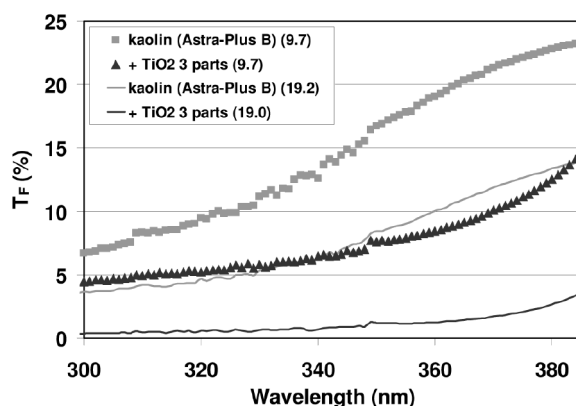


Fig 10. The transmittance factor, T_F (in the 300-385 nm region) of coating colours containing bleached kaolin clay (Astra-Plus B) and the UV-absorbing additive titanium dioxide (TiO₂). The coat weight in g/m² is given in parenthesis. More information of the pigment can be found in Table 1 and Fig 1.

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 minor decrease in transmittance for both kaolin and ground calcium carbonate pigments, especially at low coat weights. The transmittance factor of GCCs and PCCs are more or less wavelength independent over the entire region, while kaolin clays display a decrease in T_F at lower wavelengths which is beneficial for the brightness stability. It was further concluded that a narrow pigment size distribution was beneficial for reducing the amount of transmitted UV-radiation that reaches the base paper. When the binder styrene butadiene latex was exchanged for polyvinylpyrrolidone, there was no difference in transmittance factor, but when using polyvinyl alcohol as binder, the transmittance factor increased. Adding a fluorescent whitening agent to the coating colour decreased the T_F when the pigment used was GCC, and increased the T_F when the pigment used was kaolin. Combining the best pigment (kaolin clay) and the best binder (styrene butadiene latex) with titanium dioxide (3 parts), the transmittance in the UV-region could be reduced with about 90% at a coat weight of ~10g/m².

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Literature

- Andtbacka, A., Holmbom, B. and Gratzl, J.S.** (1989): Factors influencing light-induced yellowing and bleaching of spruce groundwood, 5th Int. Symp. Wood Pulp. Chem., Raleigh, NC, USA, May 22–25, Tappi Press, Atlanta, GA, USA, Vol. 1, 347–351.
- Argyropoulos, D.S., Halevy, P. and Peng, P.** (2000): Photoyellowing inhibition of bleached high yield pulps using novel water-soluble UV screens, *Photochem. Photobiol.* 71(2), 141–148.
- Bourgoing, S. and Robert, S.** (1997): Use of fluorescent whitening agents against light-induced colour reversion of high yield pulps, 9th Int. Symp. Wood Pulp. Chem., Montreal, Que, Canada, June 9–12, Canadian Pulp and Paper Association, Montreal, Que, Canada, 10.1–10.4.
- Bourgoing, S., Leclerk, E., Martin, P. and Robert, S.** (2001): Use of fluorescent whitening agents to inhibit light-induced colour reversion of unbleached mechanical pulps, *J. Pulp Paper Sci.* 27(7), 240–244.
- Bown, R.** (1997): A review of the influence of pigments on papermaking and coating, *Fundamentals of papermaking materials*. 11th Fundamental Res. Symp., Cambridge, UK, September 21–26, Pira International, Leatherhead, UK, Vol. 1, 83–138.
- Davidson, R.S.** (1996): The photodegradation of some naturally occurring polymers, *J. Photochem. Photobiol. B* 33(1), 3–25.
- El-Sadi, H., Yuan, Z., Esmail, N. and Schmidt, J. (2002): Factors affecting the inhibition of light-induced yellowing of a coated BTMP paper, *J. Pulp Paper Sci.* 28(12), 400–405.
- Fjellström, H., Höglund, H., Forsberg, S. and Paulsson, M.** (2007a): A novel method of studying the ability of a coating layer to retard the photo-yellowing of the base paper. *Nord. Pulp Paper Res. J.* 22(3), 343–349.
- Fjellström, H., Höglund, H., Forsberg, S. and Paulsson, M.** (2007b): Inhibition of light-induced brightness reversion of high-yield pulps: The UV-screening properties of coating layers containing kaolin or calcium carbonate pigments. *Nord. Pulp Paper Res. J.* 22(3), 350–355.
- Fornier de Violet, P., Nourmamode, A., Colombo, N., Zhu, J. and Castellán, A.** (1990): Photochemical brightness reversion of peroxide bleached mechanical pulps in the presence of various additives, *Cellul. Chem. Technol.* 24(2), 225–235.
- Forsskåhl, I.** (2000): Brightness reversion. In: *Forest Products Chemistry*. Edited by P. Stenius. Fapet Oy, Helsinki, Finland, pp. 278–332.
- Fossum, T., Lindahl, A., Rudström, L. and Smedman, L.** (1976): High grade graphic paper from mechanical pulp, *Pulp Paper Can.* 77(2), 53–55.
- Gellerstedt, G., Pettersson, I. and Sundin, S.** (1983): Light-induced and heat-induced yellowing of mechanical pulps, *Svensk Papperstidning* 86(15), R157–R163.
- Ghosh, T., Cogswell, D., Cunningham, A. and Raue, D.** (2002): Inhibition of brightness reversion in coated groundwood sheets: Effect of coatweight, application method and coating ingredients, *TAPPI Coating Conf.*, Orlando, FL, USA, May 5–8, Tappi Press, Atlanta, GA, USA, 11 pp.
- Gratzl, J.S.** (1985): Lichtinduzierte Vergilbung von Zellstoffen – Ursachen und Verhütung, *Papier* 39(10A), V14–23.
- Heitner, C.** (1993): Light-induced yellowing of wood-containing papers: An evolution of the mechanism. In: *Photochemistry of Lignocellulosic Materials*. Edited by C. Heitner and J.C. Scaiano. ACS Symposium Series 531, Washington, DC, USA, pp. 2–25.
- Hortling, B., Rättö, M., Forsskåhl, I. and Viikari, L.** (1993): The interaction of polyvinylpyrrolidone (PVP) and groundwood pulp, *Holzforschung* 47(2), 155–162.
- Janson, J. and Forsskåhl, I.** (1989): Colour changes in lignin-rich pulps on irradiation by light, *Nord. Pulp Paper Res. J.* 4(3), 197–205.
- Janson, J. and Forsskåhl, I.** (1996): Polytetrahydrofuran: A polymer that counteracts colour reversion, *Nord. Pulp Paper Res. J.* 11(1), 10–14.
- Johnson, R.W.** (1989): Brightness stability of mechanical pulps. Relating laboratory data to performance, *Tappi J.* 72(12), 181–187.
- Johnson, R.W.** (1991): CTMP in fine papers: On-machine surface treatments for improved brightness stability, *Tappi J.* 74(5), 209–217.
- Kringstad, K.** (1969): Degradation of wood and high-yield pulps by light, *Tappi* 52(6), 1070–1074.
- Krogerus, B. and Forsskåhl, I.** (1995): Effects of filler pigments and additives on paper yellowing, *PSC Communications* 83, Espoo, Finland: KCL Paper Science Centre, 25pp.
- Lanzalunga, O. and Bietti, M.** (2000): Photo- and radiation chemical induced degradation of lignin model compounds, *J. Photochem. Photobiol. B* 56(2–3), 85–108.
- Leary, G.J.** (1967): The yellowing of wood by light, *Tappi* 50(1), 17–19.
- Leary, G.J.** (1994): Recent progress in understanding and inhibiting the light-induced yellowing of mechanical pulps, *J. Pulp Paper Sci.* 20(6), J154–J160.
- Lehtinen, E.** (2000): Coating pigments – General. In: *Pigment Coating and Surface Sizing of Paper*. Edited by E. Lehtinen. Fapet Oy, Helsinki, Finland, pp. 61–67.
- Lindblad, G., Iversen, T., Bergenblad, H. and Rigdahl, M.** (1989): Light scattering ability as a tool to protect paper and board against photo-oxidation, *Nord. Pulp Paper Res. J.* 4(4), 253–257.
- Luo, C. and Göttsching, L.** (1991): Technologische Massnahmen zur Verringerung der licht-induzierten Vergilbung holzhaltiger Papiere. Teil 2: Schutzwirkung von Pigmentstrichen, *Wochenbl. Papierfabr.* 119(17), 635–644.
- Maily, V., Le Nest, J.F., Serra Tosio, J.M. and Silvy, J.** (1996): Yellowing of coated papers under the action of heat, daylight radiation and nitrogen oxide gas. *TAPPI Coating Conference*, Nashville, TN, USA, May 19–33, Tappi Press, Atlanta, GA, USA, 193–202.
- Minemura, N.** (1978): Control of the photo-induced discoloration of mechanical pulp with polyethylene glycol, *Mokuzai Gakkaishi* 24(8), 587–588.
- Nolan, P., van den Akker, J.A. and Wink, W.A.** (1945): The “fading” of groundwood by light. *Paper Trade J.* 121(11), 33–37.
- Pauler, N.** (2002): *Paper Optics*, AB Lorentzen and Wettre, Kista, Sweden.
- Paulsson, M. and Ragauskas, A.J.** (1998a): Chemical modification of lignin-rich paper. Part 7: Photostabilizing high-brightness aspen CTMP by combining various classes of additives and acetylation, *Nord. Pulp Paper Res. J.* 13(2), 124–131.
- Paulsson, M. and Ragauskas, A.J.** (1998b): Chemical modification of lignin-rich paper. Part 8: Effect of light source on the accelerated light-induced yellowing of untreated and acetylated high-yield pulps, *Nord. Pulp Paper Res. J.* 13(2), 132–142.
- Peng, P. and Argyropoulos, D.S.** (2000): On the interaction of UV screens with lignocellulosic matrix, *Photochem. Photobiol.* 71(2), 149–156.
- Ragauskas, A.J., Allison, L., Lucia, L.A. and Li, C.** (2001): Brightness reversion of mechanical pulps XIV: Application of FWAs for high-brightness high-yield pulps, *Solutions/Tappi J.* 84(11), 1–11.
- Reinhardt, B. and Arneberg, U.** (1988): Die Vergilbung gestrichener Papiere unter Licht und Temperatur, *Wochenbl. Papierfabr.* 116 (5), 179–184, 186–187.
- Rohringer, P. and Fletcher, I.** (1996): Spectral properties of paper treated with fluorescent whitening agents and the effects of agent application, *TAPPI Coating Conf.*, Nashville, TN, USA, May 19–22, Tappi Press, Atlanta, GA, USA, 239–251.
- Rättö, M., Forsskåhl, I., Janson, J. and Viikari, L.** (1993): Photostabilization of mechanical pulps by polyvinylpyrrolidone, *Tappi J.* 76(6), 67–70.
- Weir, N.A. and Miller, B.** (2000): Retardation of photo-yellowing of lignin-rich pulp, *Polym. Degrad. Stab.* 69(1), 121–126.
- Yuan, Z., Schmidt, J., Gilbert, D., Aspler, J., Heitner, C., Cunkle, G. and Ghosh, T.** (2003): Improving the brightness stability of a machine coated mechanical paper: A mill trial, *Int. Mech. Pulp. Conf.*, Québec City, Québec, Canada, June 2–5, PAPTAC, Montreal, Canada, 115–123.
- Yuan, Z., Gilbert, D., Schmidt, J. and Heitner, C.** (2004): Improving the brightness stability of a machine coated mechanical paper: Part 1: Laboratory evaluation, *J. Pulp Paper Sci.* 30(7), J196–J202.
- Yuan, Z., Schmidt, J., Heitner, C. and Zou, X.** (2006): Coating improves the brightness stability of wood-free coated papers containing high-yield pulp, *Tappi J.* 5(1), 9–13.

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