Spectroscopic Investigation of IJ Layer Yellowing

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Abstract

The authors have investigated the use of fluorescence spectroscopic measurements as a method for the analysis of yellowing mechanisms in accelerated ageing tests. Two model films with defined composition were used to establish the spectroscopic method. The method was then applied to samples that had undergone accelerated ageing by ozone, thermal and humidity degradation, light exposure and chemical contamination. The use of several different spectroscopic methods allowed to discriminate between optical brightener degradation, yellow stain formation and light scattering. The results were compared to those obtained form spectral densitometer measurements.

Introduction

Today's inkjet printing systems are more stable than ever and are designed to keep the image information over a long period of time. One of the limiting factors apart from colorant degradation in image stability is paper yellowing, which may appreciably change the appearance of the print. In particular, paper yellowing is often the limiting factor in the thermal aging of prints. It can also happen when prints are displayed under light or exposed to indoor pollutants.

There are several chemical causes for paper yellowing, for example the loss of optical brightener, the degradation of IJ layer components, the absorption of contaminants and the oxidation of the base paper fibers. Some yellow stain may disappear after further exposure to heat, light or pollutants, some may be persistent. The sequence of the exposure to the environmental factors has also been shown to be of importance [1].

The exact cause of yellowing is difficult to determine by CIELAB or density measurements which provide an unspecific response to any change in the spectrum. Even with absorption spectroscopy it is difficult to distinguish parallel reactions that may occur.

Most modern IJ papers contain optical brightening agent (OBA) to enhance the whiteness. Unfortunately, factors as environmental pollution (eg. ozone, nitrogen oxides, volatile organic compounds (VOC) are known to quench the fluorescence of the OBA or lead to its degradation, optical brighteners sometimes forming yellowish reaction products [1][2][3]. Most of these reaction mechanisms in IJ papers are unknown and hard to prove.

Commonly changes in paper white are measured by spectral densitometers or Lab-meters such as eg. Gretag MacBeth's Spectrolino [4]. The advantage is that they convert spectral data into CIELAB differences which are a good representation of the visually observed effects. However, when using such an equipment, the excitation of a fluorescent compound such as an OBA happens by the UV part of the measurement light source. The response is very unspecific since absorption and emission are measured together. Different parallel reactions such as the destruction of optical brighteners and the creation of yellowish by-products cannot be distinguished easily.

In this study absorption and fluorescence spectroscopy were used to get better differentiation of reactions of a set of model films. On the basis of the results, limitations of the spectral density (CIELAB) measurements are discussed.

Experimental Setup

The study used two nanoporous model inkjet layers, one layer containing optical brightener (OBA), the other identical but without OBA (see Table 4). Both layer variants were coated on transparent polyester base. This allowed the observation of changes without interference of potential OBA effects originating from the paper base. The transmission mode of the absorption spectra gives direct quantitative data of colored components

All test samples were allowed to equilibrate in ambient conditions for four weeks after production before they were submitted to the ageing test.

Measurements were made 1 hour and 24 hours after the test. Only the 1 hour results are shown in the paper. The CIELAB and Dmin (Status A) data are based on spectral densitometer measurements which were made in remission density backed by the calibration tile with a Gretag MacBeth Spectrolino using two different conditions. Condition A was a measurement without additional filters and thus with some UV light. In condition B the UV part of the spectral densitometer light source was filtered out (cutoff wavelength 390nm). The detailed settings used are listed in table 1.

Table 1: Gretag MacBeth Spectrolino settings

	A	B
Illumination	D65	D65
Filter	No	UVcut
Underlay	$BaSO_4$ tile	$BaSO_4$ tile
Measurement	densities, Cie Lab, spectrum R	

The absorption spectroscopic measurement was done by means of a UV-VIS Spectrophotometer Varian Cary Bio 100 (settings see table 2) in transmission. The fluorescence emission and excitation measurements are made by a Varian Cary Eclipse equipment (settings see table 3).

Table 2: Settings Varian Cary Bio 100

Wavelength	[nm]	320-750
Baseline correction		Yes
Double beam mode		Yes

Table 3: Settings Varian Cary Eclipse

		Emission Sp.	Excitation Sp.
Excitation wavelength	[nm]	345	200-400
Excitation slit	[nm]	5	
Detector slit	[nm]	5	
PMT detector voltage	[V]	600	
Detector, wavelength	[nm]	355-650	Fixed to eg 410

Table 4: sample set

Sample	Type	OBA	Description
T0	transparent	No	PE film base
T1	transparent	No	nanoporous silica layer on PE film
T2	transparent	Yes	nanoporous silica layer on PE film

The samples were exposed to different accelerated ageing tests with the conditions shown in table 5. The tests were done to generate yellowing in the unprinted layers by different forms of environmental degradation and to investigate the usefulness of the fluorescence spectroscopic measurements in the prediction of print ageing.

Table 5: accelerated ageing tests done with the sample set

description	Conditions
Light exposed	10 Mluxh (exposed in ATLAS ci-35)
Heat exposed	5d/12d at 60°C (in gas tight boxes)
Humidity exposed	14 days at 26°C / 80%rh, free hanging
Ozone exposed	84 ppmh (84h at 1ppm)
Heat & rubber exposed	sample + rubber material in gas tight boxes for 5d at 60°C

The light exposure was done using an Atlas ci-35 equipment with settings as shown in table 6.

Table 6: Light exposure settings

Light intensity	[klux]	75
Ambient temperature	[°C]	30
Humidity	[%]	50
Exposure	[Mluxh]	10

The ozone exposure test was done in a Hampden ozone cabinet model 903 using parameter settings as shown in table 7.

Table 7: Ozone exposure settings

Ozone conc.	[ppm]	1.0
Temperature	[°C]	30
Humidity	[%]	50
Air flow	[l/min]	200
Exposure	[ppmh]	84

Results

Spectroscopic Investigation of Unexposed samples

Fig. 1 shows the spectral densitometer curves of the unexposed references used in the Delta CIELAB and Delta Dmin calculations. By measuring with and without UV filter it is possible to detect the effects of fluorescent substances such as OBA.

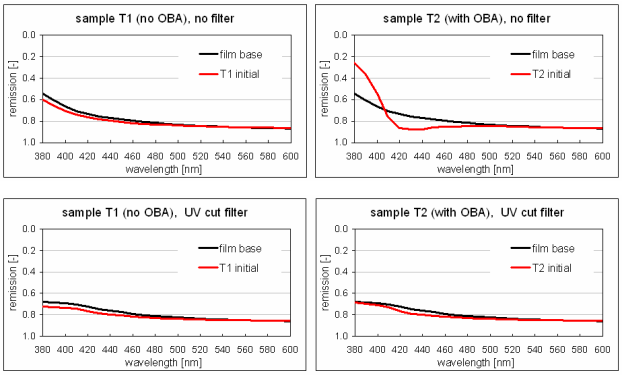

Figure 1. *Spectral densitometer remission density (Spectrolino) for top left: sample T1 / no filter top right:sample T2 / no filter bottom left: sample T1 / UV cut filter bottom right: sample T2 / UV cut filter*

For the sample T1 with no OBA the remission density curve is close to that of the clear film base. For the sample containing OBA, T2, the measurement with and without UV cutoff filter are different. In the case of the measurement without a filter, some UV light is present and UV absorption of the OBA can be observed up to 410 nm. In the region of 410-500 nm the remission is higher than that of the clear film base alone. This effect indicates the fluorescent emission of the OBA.

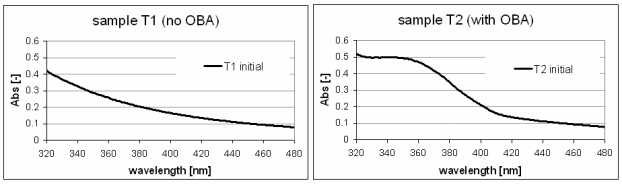

Figure 2. *UV/VIS Absorbance Spectrum for sample T1, T2*

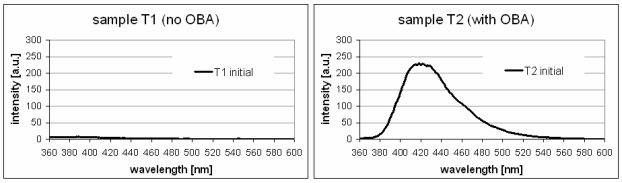

Figure 3. *Fluorescence Emission Spectrum for sample T1, T2*

Compared to UV/VIS absorbance spectroscopy (Fig. 2) and fluorescence emission and excitation spectroscopy (Fig. 3) the resolution of spectral densitometers is lower and limited to a

wavelength of 380nm and higher (Fig. 1). Effects in the lower UV range can therefore not be detected.

Both standard UV/VIS absorption and fluorescence emission spectra show clearly that sample T1 does not contain OBA. Therefore the absorption curve corresponds to the absorption of the raw film base which shows the typical scattering behaviour of a nanoporous layer. Sample T2 contains OBA which absorbs in the wavelength range up to 410nm and emits from 380-530nm with a maximum at about 420nm.

Spectroscopic measurement of exposed samples

Light exposed samples

Table 8: Spectral densitometer measurement of 10Mluxh exposed samples T1 and T2

Sample T1		Sample T2	
$dDmin_{blue}$ (no filter)	-0.007	$dDmin_{blue}$ (no filter)	0.031
$dDmin_{blue}$ (UV cut filter)	-0.004	$dDmin_{blue}$ (UV cut filter)	0.007
dE (no filter)	0.51	DE (no filter)	2.84
dE (UV cut filter)	0.45	DE (UV cut filter)	0.14

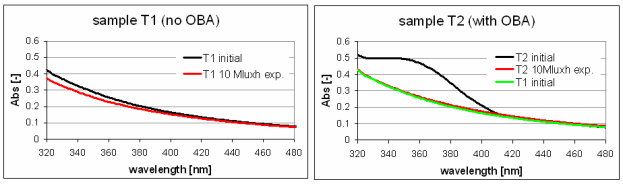

Figure 4. *UV/VIS Absorbance Spectrum for sample T1 and T2*

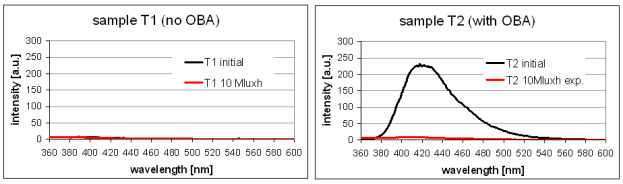

Figure 5. *Fluorescence Emission Spectrum for sample T1 and T2*

The film layer without OBA shows very little difference between the unexposed reference and the exposed sample while the film layer with OBA shows full degradation of the OBA including the UV absorption band. No formation of side products can be observed (Table 8, Fig. 4, 5).

Heat exposed samples

Table 9: Spectral densitometer measurement of samples T1 and T2, exposed 5d and 12d to 60°C

Sample T1	5d	12d	Sample T2	5d	12d
$dDmin_{blue}$ (no filter)	0.002	0.008	$dDmin_{blue}$ (no filter)	0.010	0.020
$dDmin_{blue}$ (UV cut fi.)	0.004	0.011	$dDmin_{blue}$ (UV cut fi.)	0.010	0.010
dE (no filter)	0.40	0.87	dE (no filter)	0.67	1.80
DE (UV cut filter)	0.47	0.96	dE (UV cut filter)	0.36	0.77

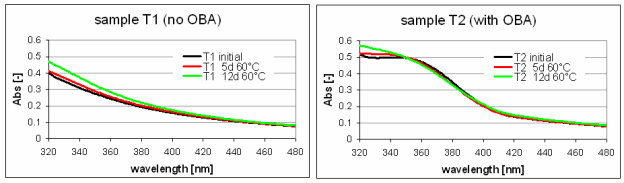

Figure 6. *UV/VISAbsorbance Spectrum for sample T1 and T2*

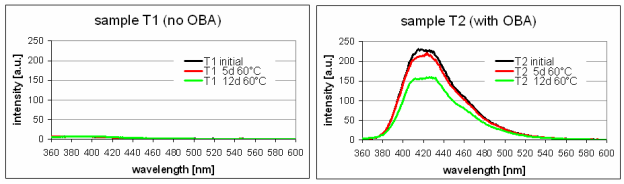

Figure 7. *Fluorescence Emission Spectrum for sample T1 and T2*

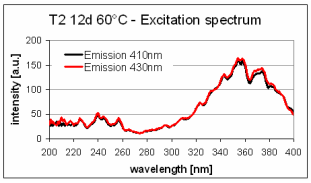

Figure 8. *Fluorescence Excitation Spectrum for sample T2, 12d 60°C*

The thermal tests were done for two durations, one for 5 days and one for 12 days. Several reactions seem to occur. In both layers, an increase in the UV-absorption below 340nm can be observed. The fluorescence spectra shows that in sample T2 the OBA is partially destroyed or quenched. As the shape of the fluorescence peak changed slightly, it was suspected that two or more by-products might have formed. The diagnostic fluorescence excitation spectrum run on the same sample suggests however, that the observed fluorescence is due to only one compound (Table 9, Fig. 6, 7, 8).

Humidity exposed samples

Table 10: Spectral densitometer measurement of samples T1 and T2, exposed to 26°C and 80%rh for 14 days

Sample T1		Sample T2	
$dDmin_{blue}$ (no filter)	-0.001	$dDmin_{blue}$ (no filter)	0.000
$dDmin_{blue}$ (UV cut filter)	0.000	$dDmin_{blue}$ (UV cut filter)	0.010
dE (no filter)	0.22	DE (no filter)	1.30
dE (UV cut filter)	0.30	DE (UV cut filter)	0.19

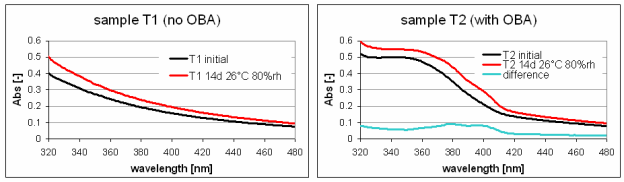

Figure 9. *UV/VIS Absorbance Spectrum for sample T1 and T2*

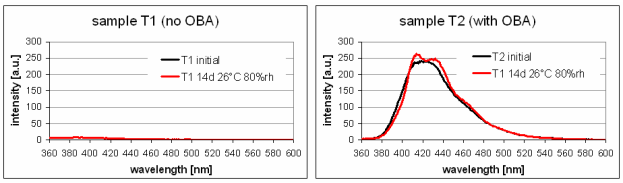

Figure 10. *Fluorescence Emission Spectrum for sample T1 and T2*

A general increase of sample absorbance can be seen after exposure to high humidity (Table 10, Fig. 9, 10). The reference sample T1 shows an increase that can be attributed to enhanced scattering, whereas the absorption spectrum of T2 additionally shows the presence on a newly formed compound (see difference spectrum in Fig. 9). Structural changes in the nanoporous layer could account for the enhanced scattering. The fluorescence emission spectrum does not show a loss in fluorescence, but a change in the form of the peak, which could indicate a change of the OBA environment. The absolute fluorescence intensity should be interpreted with caution in this case, because it might be influenced by the different scattering behaviour of the sample. The difference spectrum of the absorption, however, confirms that there is no major decomposition of the OBA (see also Fig. 16). It was not the aim of the study to investigate if the effect is reversible after more than 24h.

Ozone exposed samples

Table 11: Spectral densitometer measurement of samples T1 and T2, exposed to 84 ppmh O_3

Sample T1		Sample T2	
$dDmin_{blue}$ (no filter)	-0.001	$dDmin_{blue}$ (no filter)	0.030
$dDmin_{blue}$ (UV cut filter)	0.001	$dDmin_{blue}$ (UV cut filter)	0.008
dE (no filter)	0.13	DE (no filter)	2.93
dE (UV cut filter)	0.11	DE (UV cut filter)	0.08

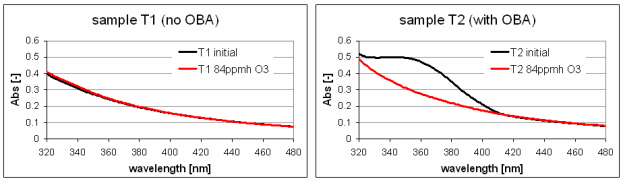

Figure 11. *UV/VIS Absorbance Spectrum for sample T1 and T2*

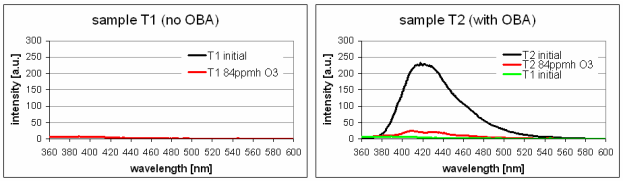

Figure 12. *Fluorescence Emission Spectrum for sample T1 and T2*

The exposure to ozone does not seem to have any effect on the layer without OBA. However, the OBA is nearly completely degraded in film T2 after 84ppmh of ozone exposure similar to typical IJ imaging dyes. As for light exposure the UV chromophore is completely destroyed (Table 11, Fig. 11, 12).

Heat and rubber exposed samples

Table 12: Spectral densitometer measurement of samples T1 and T2, exposed 5d to 60°C together with rubber

Sample T1		Sample T2	
$dDmin_{blue}$ (no filter)	0.039	$dDmin_{blue}$ (no filter)	0.069
$dDmin_{blue}$ (UV cut filter)	0.042	$dDmin_{blue}$ (UV cut filter)	0.057
dE (no filter)	4.37	DE (no filter)	6.84
dE (UV cut filter)	4.43	DE (UV cut filter)	5.14

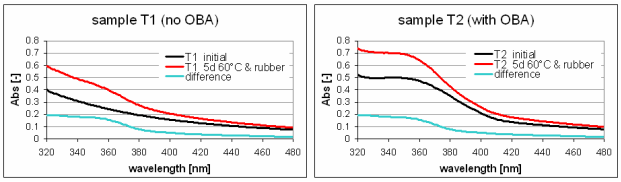

Figure 13. *UV/VIS Absorbance Spectrum for sample T1 and T2*

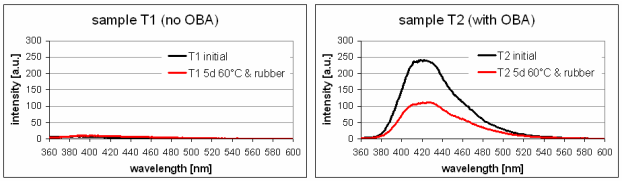

Figure 14. *Fluorescence Emission Spectrum for sample T1 and T2*

The simultaneous exposure to heat and rubber produces an increase of the absorption in the UV and yellow part of the spectrum in both layers. The slightly yellowish compound produced is not dependent on the presence of the OBA and identical for both layers.

However, the fluorescence of the OBA containing layer is appreciably more reduced in the presence of rubber than it was after the 5 days high temperature test alone. This could be due to the quenching of the fluorescence by compounds from the rubber, the competing absorption of UV light of the newly formed compound or a chemical reaction between OBA and the newly formed compound (Table 12, Fig 13, 14).

Difference UV/VIS spectra for all exposed samples

The difference absorbance spectra of Figure 15 show very nicely if during a certain treatment the absorption is reduced (negative values) or on the other hand additional absorption exists (positive values). Light and ozone treatment obviously destroy the OBA in T2, but do not have a major effect on the samples T1 without OBA. The heat treatment does only slightly destroy the OBA in T2, but an additional absorption below 340 nm is building up in both layers T1 and T2. The humidity treatment leads to some increased scattering in T1. In T2 there is clearly an additional absorption spectrum of a new substance appearing that will cause yellowing due to its absorption tail above 400 nm. The rubber treatment obviously leads to an increase in absorption of both samples T1 and T2, which indicates that the source of this absorption is due to the rubber and has probably nothing to do

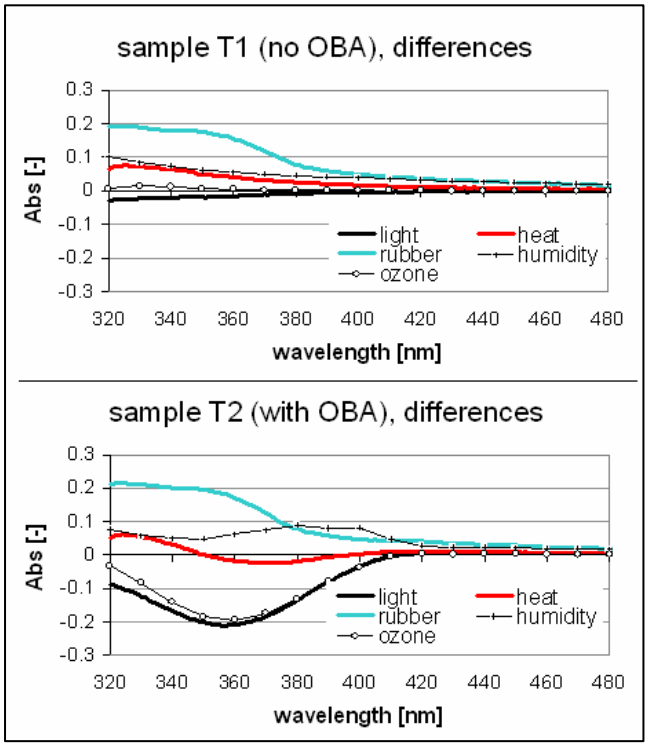

Figure 15. *Difference UV/VIS Absorbance spectra for sample T1 and T2 where the spectra of the initial samples are substracted from the spectra after the indicated treatments to show the induced spectral changes*

with the OBA. The absorption has two components: a strong absorption below 380 nm and a weaker one above 380 nm that reaches into the visible (>400 nm) and therefore causes a yellow color of the layers.

Conclusion

The study showed that it is possible to distinguish between different mechanisms leading to yellowing by combining fluorescence spectroscopy and absorption spectroscopy. The spectral densitometer measurement represents the overall visual effect and compares well when only one type of degradation occurs. However, it cannot distinguish between different yellowing mechanisms such as the degradation of the OBA and the simultaneous forming of yellowish stain and is of limited value when elucidating different forms of yellowing. The study also confirmed that the OBA in nanoporous IJ layers is a rather unstable compound and is quite easily degraded by ozone, light and heat. Humidity alone at ambient temperature is less degrading. The light and ozone test were only run up to conditions that would represent less than 10 years of unprotected image display under average home conditions (250 Lux for 12h/d, 40 ppmh ozone per year). The visual change in white after complete OBA destruction will normally not reach the end point limits for Dmin. However, if yellowish by-products are formed or contaminants are present, the combined effects may reach those limits [5].

The result of the experiments have also shown that the combination of absorption and fluorescence spectroscopic investigations offers potential for examining fundamental mechanisms in the ageing of IJ layers.

Especially for real life effects caused by multiple factors simultaneously acting on a print, fluorescence spectroscopic investigations could be of help to investigate mechanisms.

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Author Biography

J. Reber studied chemistry at Burgdorf University of Applied Science in Switzerland. He worked for several years in analytical chemistry as a test engineer and group leader in a private service laboratory. In 2003 he joined ILFORD and has been workings in the field of image science and performance in research and development. The focus of his activities is in test methods and result characterization for inkjet media.