

# Activation Energy of Dye Degradation Processes on Different Inkjet Papers

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## Abstract

Understanding light- and storage stability is of utmost importance in inkjet printing. In this paper we present investigations of light-induced kinetics of dye degradation. Magenta, black and cyan dyes are irradiated on typical glossy and matt media using a Xenon lamp and the decrease of remission intensity with irradiation time is recorded using UV-Vis spectroscopy. Most dye kinetics can be described as 1<sup>st</sup> order reaction at least in the beginning of the reaction. From temperature dependence of 1<sup>st</sup> order kinetics we are able to determine activation energies for the decay process allowing us a detailed media-dependent comparison of kinetic behaviour. Furthermore an analysis of UV-Vis spectra show that not only one single degradation channel is responsible for light fading processes.

In order to define the contribution of oxidative non-light induced processes UV-Vis data of dark storage under oxidative atmosphere are compared in shape and intensity allowing a separation of light and oxidative decay channels. For most ink-paper combinations a superposition of light-induced and oxidative mechanisms are likely. Using activation energies as parameter for dye-paper stability also the influence of room humidity on stability of inkjet prints can be estimated.

## Introduction

Light fastness is one of the most important item in inkjet printing today. After photographic quality has been almost reached by inkjet technology customer attention was conducted to the light fastness of these prints becoming important when pictures are stored under various conditions for a longer time. For highly stable prints and for outdoor applications pigmented inks are used however due to higher brilliance, better compatibility and higher colour gamut dyes are still favourites for photo realistic inkjet prints.

Degradation of dyes is known to depend on a wide variety of environmental parameters like temperature, humidity,<sup>1</sup> light intensity and spectral distribution explaining why it is difficult to provide exact data for lifetime of inkjet prints. There are a lot of investigation and empirical explanations known in the literature how dye degradation may take place and which are the most probable degradation channels.

A lot of research work has been done in the past with focus on changes in CIE Lab- or density figures<sup>2</sup> with light irradiation, which is of importance mainly for practical use.<sup>3</sup> Beside light induced changes especially microporous paper is known to suffer from air pollutants like ozone and NO<sub>x</sub>.<sup>4</sup> Certainly the separation of contributions from light or from oxidising agents is difficult if both reactions occur parallel. Further from a scientific point of view changes in density of CIE Lab-figures are not suited to conclude or determine physical parameter associated with degradation reactions.

The activation energy as key kinetic parameter has not been determined yet in dependence from media and dye. In this article we present investigations of activation energies on different media with different dyes also considering the influence of room humidity. Because of possible interference with light-induced decay channels we include storage tests under highly oxidative atmospheres in our investigation. By comparing the shape of the remission spectra we were able to distinguish between both mechanisms.

## Experimental

Using an Epson 1290 inkjet printer colour targets were printed with full colour (100%) and 40%-areas on two types of media. Tetenal 264g was chosen as representative for a high glossy paper with microporous coating and Tetenal Duoprint as a typical matt surface. As inks Tetenal spectra inks were used replacing the dye components by Direct Red 75, Food Black 2 and Direct Blue 199. For irradiation an Atlas sun-tester CPS+ with Xenon irradiation is used. The print samples were deposited in a closed box with window glass as filter (simulating indoor conditions). The temperature of this box was adjusted by a water bath; room humidity was adjusted using an open dish with saturated salt solutions within the sample box. To reduce sample heating the irradiance intensity was reduced to 400 W/m<sup>2</sup>, overall irradiation time was 80 hour. Every 8-hour of irradiation remission spectra were recorded using a Gretag Spectrolino. Remission spectra were recorded from 380 nm to 750 nm in 10 nm steps.

Dark storage tests with oxidizing atmosphere were performed under exclusion of light at 60°C for an overall test time of 80 hours in a closed box with 30% H<sub>2</sub>O<sub>2</sub>-solution.

## Results

### Remission Spectra During Irradiation

In Fig. 1 the time dependence of a black dye on matt paper as a function of irradiation time is shown. Already after 8 hours under 86% room humidity a strong decrease in the absorption band around 600 nm can be observed. The relative decrease in intensity for 600 nm and 410 nm is obviously different indicating a superposition of two processes.

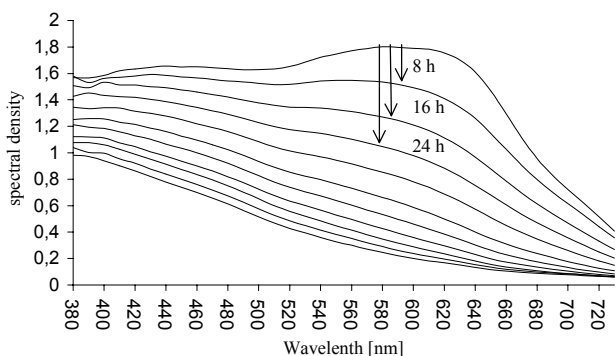


Figure 1. Time dependent light induced decrease of remission intensity of black dye on Tetenal Duoprint matt paper

Identification of side reaction is possible when remission intensities are plotted at two different wavelengths on x- and y-axis. In case that only one reaction takes place the plot should exhibit a linear correlation. The diagram is shown in Fig. 2 indicating a linear relation for the first irradiation periods however after longer irradiation time a clear deviation points to a second reaction.

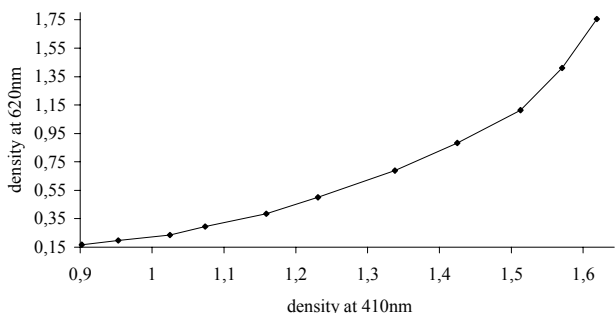


Figure 2. Relation between remission at 410 nm and 620 nm during irradiation of black dye on Tetenal Duoprint matt paper

Whereas for the black dye no hint is found for a single reaction pathway for magenta isosbestic points are observed in the beginning of the irradiation for full colour areas (100%) as well as for 40% where the effect is even more clearly (Fig. 3). Isosbestic points at 410 nm and 470 nm show that in the beginning only one reaction pathway is responsible for the degradation of magenta. However, similar to the black dye after longer irradiation obviously a slower degradation reaction becomes dominant so that the

isosbestic point disappears after about 24 hours of irradiation.

In the beginning of irradiation tests a new absorption band is built between 410 nm and 470 nm as a reaction product of light induced degradation of magenta. The absorption band can be calculated as difference of remission spectrum at  $t = 0$  and remission spectrum at  $t = 24$  hours irradiation time (inset in Fig. 3).

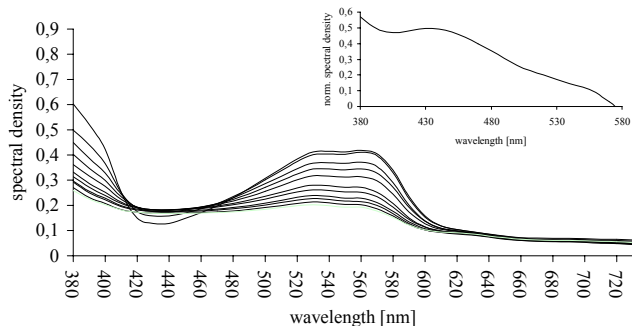


Figure 3. Remission spectra of magenta light on Tetenal Duoprint matt paper

### Determination of Activation Energies

Taking into account the above mentioned side reactions the activation energy was calculated neglecting data at higher irradiation times. For the black dye the assumption of an 1<sup>st</sup> order reaction fits very well the measured data (Fig. 4).

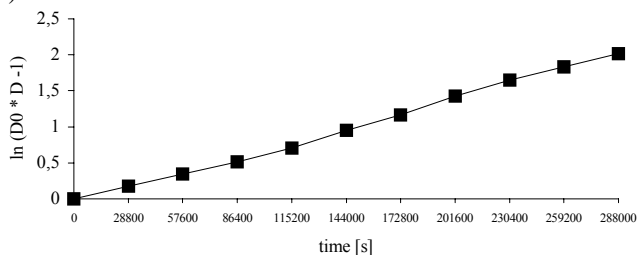


Figure 4. Plot of first order reaction  $\ln(D_0 * D^{-1})$  against time for the black dye on Tetenal Duoprint matt paper

Measuring the kinetics at different temperatures it is possible according to Arrhenius to determine the activation energy as the slope of  $\ln(k)$  against  $T^{-1}$  (Fig. 5).

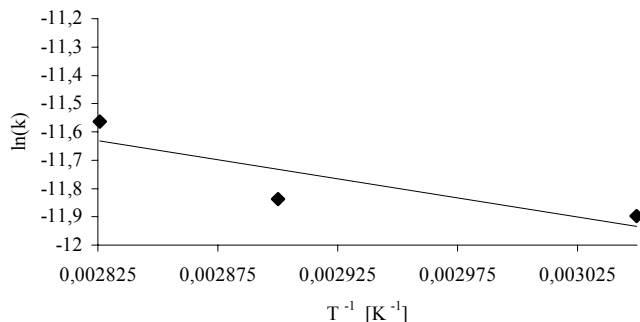


Figure 5. Plot of  $\ln(k)$  against  $T^{-1}$  to determine the activation energy of black dye on Tetenal Duoprint matt paper

For black and magenta reasonable figures could be obtained whereas the cyan dye is too stable to allow the determination of activation energies under these experimental conditions. On the other hand, because the cyan remission spectra almost does not change during irradiation and the maximum of magenta remission spectra is in the rising edge of the cyan band (540 nm) it is possible to extract the activation energies for magenta in print samples of blue as difference of remission spectra from magenta and cyan at 540 nm (Fig. 6).

This is of special interest because dyes are known to fade at different reaction speeds depending on whether they are combined with other colours or not.

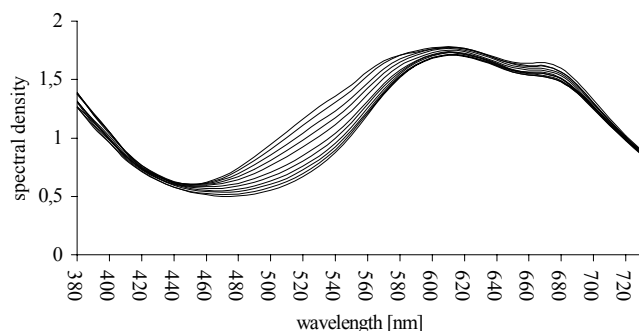


Figure 6. Remission spectra of blue on Tetnal Duoprint matt paper.

Following the explained procedure from remission spectra for different dye and paper combinations we determined the activation energies listed in Table 1.

Table 1 shows that as expected media composition has a basic influence on activation energy. For all dyes the activation energy is lower for TETENAL duoprint paper matt paper meaning a lower stability of dyes printed on matt paper. It is interesting that although micropore paper is known to react more sensitive to dye degradation our investigations show a higher stability of dyes on Tetenal 264g micropore paper. This is of course only true in case that light-induced reactions are the only fading mechanisms in absence of higher concentrations of oxidative gases.

Also, the activation energies in Table 1 show that the dye concentration influences the stability of the print. Higher dye concentration (100% areas are printed with full magenta, 40% areas with magenta light) exhibit higher activation energies on both matt paper and micropore coatings. This confirms results in literature where concentration dependent fading rates were reported.<sup>5</sup>

Room humidity plays a minor role; generally higher humidity lowers activation energies slightly.

One effect, which is known as catalytic fading, is also supported by this investigation. Comparing activation energies from magenta and blue (magenta and cyan) the combination with cyan destabilises magenta leading to lower activation energy in the secondary colour compared to magenta alone.

Table 1. Activation energies for different ink – media combinations

Colour	Media	Room Humidity [%]	$E_a$ [kJ mol <sup>-1</sup> ]
Black	Duoprint matt	86 %	11,1
		33 %	10,4
Black	Micropore glossy	86 %	20,2
		33%	22
Magenta	Duoprint matt	86%	26,42
		33%	17,7
		86%	31,3
	Micropore glossy	86%	52,6
		33%	11,71
		33%	19,2
Magenta light	Duoprint matt	86%	15,8
		33%	25,4
		86%	6,1
Magenta (blue)	Duoprint matt	33%	12,5
		86%	16,53
		33%	27
Magenta light (blue)	Duoprint matt	86%	7,3
		33%	19,8
		86%	14,4
	Micropore glossy	33%	10

### Interference of Side Reactions

One precondition for determination of activation energies in inkjet systems was the possibility to separate side reactions from light induced dye degradation. Otherwise the activation energy would reflect an average value for different decay channels. Analysing the shape of e.g. magenta spectra on matt paper we observed two isobestic points during first stage of degradation indicating that only one decay mechanism is responsible for the dye degradation. These isobestic points disappeared after further irradiation and the complete remission band decreases in intensity pointing to an additional decay mechanism.

It is worth to compare the shape of remission spectra of magenta on matt paper obtained for dark storage periods with the spectra of light induced investigations. Within the first irradiation period the remission increases in the wavelength area of about 420-460. In case of dark storage under oxidative atmosphere the complete remission spectra decreases in intensity similar to the behaviour of light induced degradation at longer irradiation times. Both time dependencies are compared in Fig. 7. The decrease and shape of remission spectra at longer irradiation times can be simulated using dark storage tests under oxidative atmosphere.

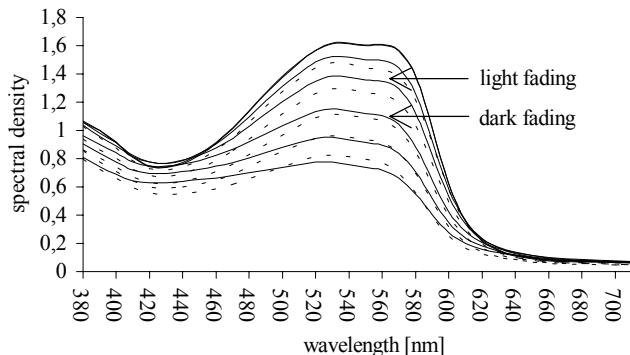


Figure 7. Comparison of remission band shape of Magenta on Tetenal Duoprint matt paper: a) dark fading under oxidative atmosphere, b) light fading

These results point to a superposition of two different mechanisms for magenta a) light induced degradation with formation of a remission band at 440 nm and b) an oxidative mechanism which is dominant at dark fading and plays a major role at longer irradiation times.

### Summary

Light induced changes in remission spectra can be used to determine activation energies for different dye-paper combinations. The calculated activation energies allow an estimation of impacts of different environment parameters like room humidity, influence of media and catalytic fading. Analysis of remission intensity decrease points to side reactions during the irradiation which become dominant on a larger time scale of irradiation. The origin of these side reactions is attributed to oxidative non-light induced degradation pathways. From shape analysis of remission curves we conclude that the degradation of dyes is a superposition of light induced reactions and oxidative pathways.

### References

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### Biography

**Dr. Umberto De Rossi** studied chemistry and received his Ph.D. in physical chemistry at the Free University in Berlin in 1996. After a post-doctorate at the Max-Planck Institute of Surface and Colloid Science Dr. De Rossi joined Tetenal and worked on photographic chemistry. Parallely he established a research division for inkjet inks and papers and is currently head of R&D at Tetenal. Dr. De Rossi holds several patents and scientific publications.