Photochemical Studies on the Lightfastness of Ink-Jet Systems

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Abstract

Model experiments using a flow photoreactor (Hg-immersion lamp) connected to a spectrophotometer are useful to study the influence of the state of dye aggregation and of certain addenda on lightfastness. Such experiments can be carried out in the transmission- or in the diffuse reflectance mode (ULBRICHT integrating sphere), the latter being useful for diffuse particulate systems with agglomerates of AlOOH nanoparticles. Such measurements can often be correlated with results in ink-jet receiving layers. Parameters like humidity, temperature, solvents, polymers etc. in ink receiving layers or in inks are shown to influence photolysis by the state of dye aggregation.

While we could show that a ***photoreductive*** radical mechanism is responsible for certain dyes, ***photooxidation*** was observed for other dyes in the **same** ink receiving layers. The presence of certain dyes in multicolor dots sometimes promotes a triplet-sensitized **photocatalytic oxidation** which depends on the state of dye aggregation, the chemical structure of the dye and on the presence of certain addenda in ink-receiving layers. Our experiments have shown that no single, well defined mechanism is responsible for the photodegradation of ink-jet dyes. Therefore, no single process is responsible for the photostabilizing action of additives.

Introduction

In a *previous paper*[1], we have shown that the light fastness of ink-jet prints depends on the composition of the inks (dyes, solvents etc.) as well as that of the receiving layers (e.g. gelatin, polymers etc.). In addition, the environment used for storage of prints (temperature, humidity) and the spectral composition of the light source were shown to influence the light stability of prints. In the *present paper* we discuss some *mechanisms* which are relevant for the photolysis of printed pictures. Conclusions are drawn from photolysis of ink-jet dyes in **aqueous solutions** and from measurements of their light-fastness in **ink-jet prints**. Aggregation equilibria of ink-jet dyes are shown to be important for a better understanding of light-fastness.

Fig. 1 shows the absorption spectra of a magenta ink-jet dye in aqueous solution, which is destroyed by photo-oxidation, as a function of exposure time to the mercury lamp of the photoreactor (full emission spectrum, quartz vessels). The two absorption maxima correspond to different extents of dye aggregation.

Dye Photolysis in Aqueous Solutions

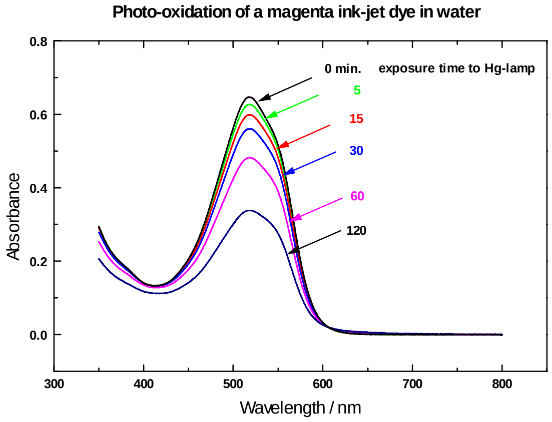


Figure 1.

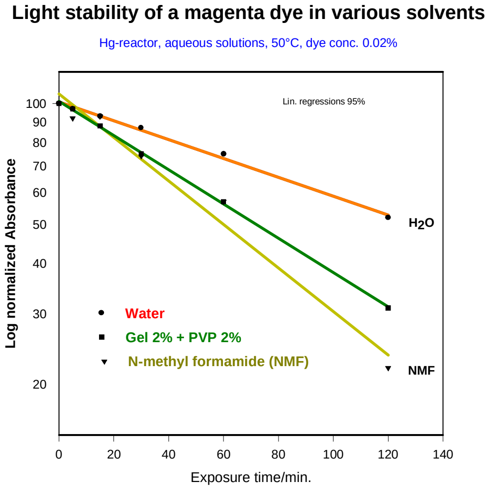


Figure 2.

Replacing pure water by various solvents (e.g. Polyvinyl-pyrrolidone PVP in a 2% aqueous gelatin solution, or pure N-methyl-formamide NMF, **Fig. 2**), a pseudo first order plot of the normalized absorbance vs. exposure time shows the influence of these solvents on the kinetics of irreversible dye destruction. The presence of PVP in aq. gelatin or NMF instead of water decreases the lightfastness of the dye as compared to pure water or aqueous 2% gelatin.

As the absorption spectra present the highest state of dye aggregation in pure water and the lowest in pure NMF (**Fig. 3**), we expect that increased dye aggregation should stabilize the dye against photolysis.

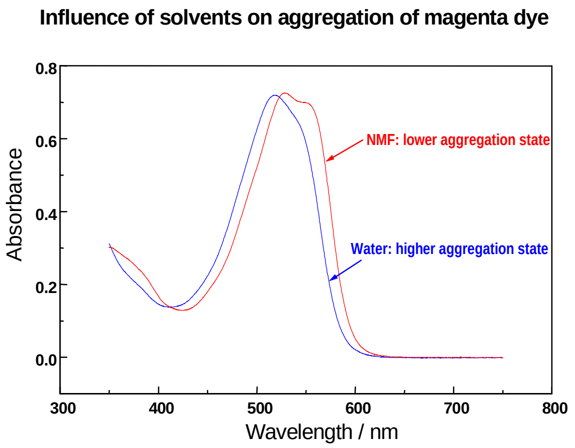


Figure 3.

In fact, the addition of NMF or glycols (10 vol%) to aqueous inks of this dye was shown to decrease the lightfastness of ink-jet **prints** drastically. The lowest light stability was found with inks containing NMF or tetraethylene-glycol. Increasing the number of ethylene groups in glycols decreased the light-stability in these prints. As shown in absorption spectra of this dye in aq. solutions enriched with these solvents (**Fig. 4**), this effect can be explained by decreased dye aggregation due to the solvents. Starting dye deaggregation is detected already in water containing only 2.5 vol.% of NMF. This shows how critical certain solvents may be for photolysis.

An increasing number of ethylene groups in glycols (leading to enhanced hydrophobicity) decreases the state of dye aggregation, **Fig. 4**. The absorption spectra of the dye have their maxima at identical wavelengths in aq. solutions and in printed magenta areas. Therefore, the same type of dye aggregates is formed in prints. These results show that photolysis of ink-jet dyes in solution may help to understand lightfastness of dyes in prints. Quantitative understanding is easier from spectra in solution, as these show differences due to dye aggregation more clearly than spectra of printed dye areas. They can be deconvoluted into higher- and lower aggregation states and, after integration, plotted semi-logarithmically vs. wavenumbers. This often leads to pseudo first-order plots (which are due to the fact that the number of incident photons is high compared to the dye concentration and can be therefore considered as constant).

Solution measurements in the **diffuse reflection mode** are useful to study the light-fastness of ink-jet dyes adsorbed on mesoporous, nanocristalline metal oxides. After corrections of the measured spectra by KUBELKA-MUNK equations, these spectra can be quantitatively evaluated as absorption spectra. **Fig. 5** shows an example for the photooxidation of a magenta dye which is adsorbed on nanocristalline pseudo-BOEHMITE (AlOOH) in aqueous, diluted solution of the dye.

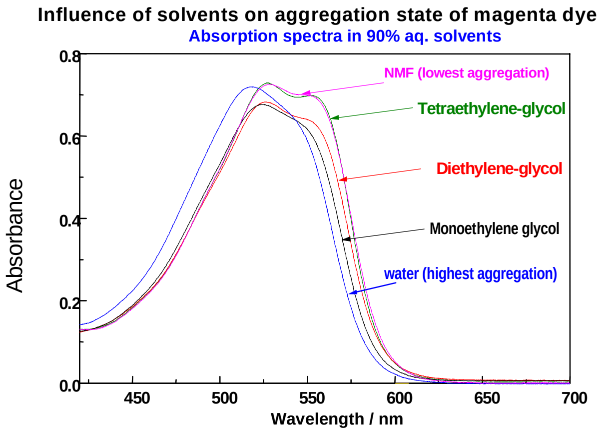


Figure 4.

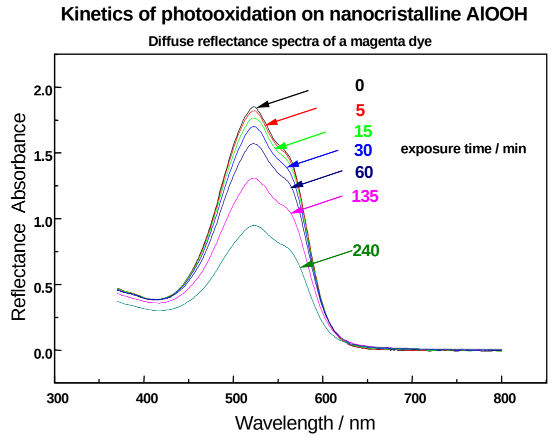


Figure 5.

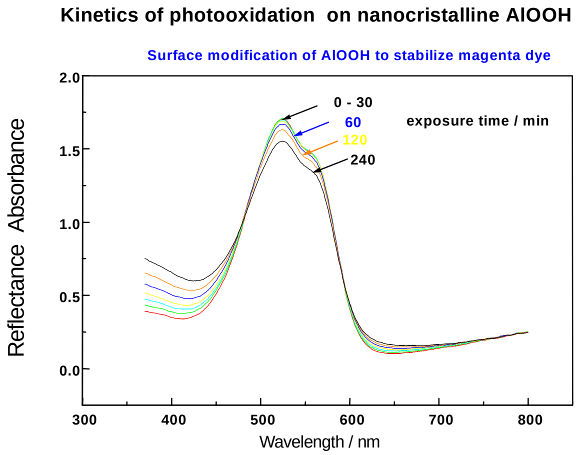


Figure 6.

Surface modification by addenda and their influence on photolysis and dye aggregation can easily be followed by this type of measurements, **Fig. 6**. As the spectra reveal the same relative contribution of absorption maxima as without the addenda, the stabilizing effect is not due to enhanced dye aggregation.

Lightfastness of Ink-Jet Dyes in Prints

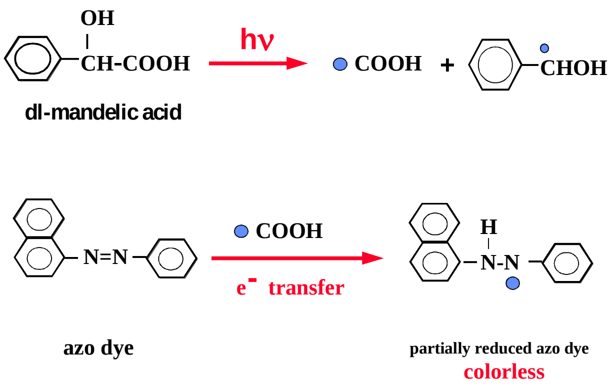
As mentioned above, the influence of dye aggregation on the lightfastness in prints was studied by adding solvents to the inks. Another technique consisted in using receiving layers containing compounds which influence dye aggregation. PVP, other polymers, and certain cellulose derivatives showed drastic decrease of dye light-fastness by their deaggregating properties.

However, the light-fastness of ink-jet dyes is too complex to be explained by dye aggregation alone. In order to understand by which **mechanisms** dyes are destroyed, we have carried out studies on printed layers containing various photo-active compounds coated in the media. Such studies lead to the conclusion that no single, well defined mechanism can explain the photodegration of ink-jet dyes in prints.

While certain dyes are destroyed by **photoreduction**, other dyes can be **photo-oxidized** or destroyed by **photo-catalysis** *in the same media.*

The most probable mechanism for the **photo-reduction** of an azo dye, based on the addition of radical formers (e.g. mandelic acid) or quenchers to our receiving layers, is given below. It is based on published results[2] using dl-mandelic acid as a radical former.

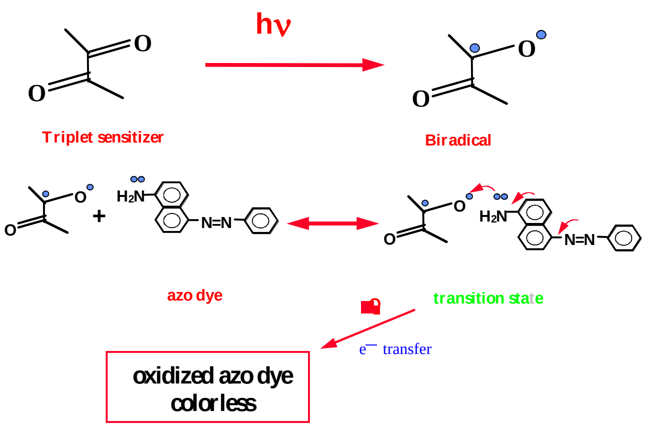
Photo-Reduction of azo dyes



The addition of this radical and other radical formers to our layers decreased the light-fastness of a magenta azo dye, destroyed by photo-reduction, very drastically, in agreement with this mechanism.

By jetting an azo magenta ink-jet dye having a *different molecular structure* on the **same receiving layers**, these radical formers had no effect. However, the addition of addenda influencing the dye triplet state (e.g. triplet quenchers like histidine or L-tyrosine) increased the light fastness of this dye. From experiments with a large number of various photo-active addenda in coatings, a triplet sensitized photo-oxidation mechanism was found to be most probable, in agreement with published results[3,4]:

Triplet-sensitized photooxidation of azo dyes

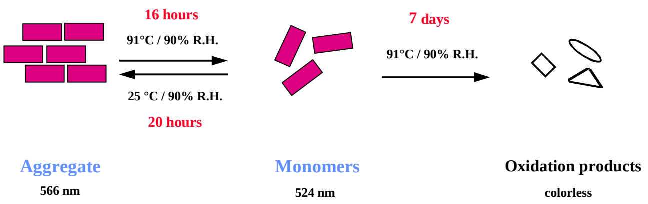


The given mechanism[3,4] was derived from studies using biacetyl triplet sensitizers for the photo-oxidation of azo dyes. Inhibition by triplet quenchers and increased dye stability was shown in these studies, in agreement with our results in coated and printed media. In some cases, we could show that certain dyes may act as triplet sensitizers for other dyes in multi-colored areas leading to enhanced dye destruction as compared to monochrome areas. This **photocatalytic** oxidation of azo dyes, triplet sensitized by other dyes (e.g. phtalocyanines), was shown to depend on the state of aggregation of **both** dyes. The action spectrum of photolysis was that of the triplet-sensitizing dye.

Aggregation Equilibria

The following scheme, which shows our results on aggregation equilibria of a typical magenta azo dye in the *absence of light*, may help to understand why aggregates are so important for dye photolysis. Absorption spectra were taken from magenta dye areas on transparent base containing gelatin coatings.

Aggregation equilibrium for a magenta azo-dye



In the case of this dye, 22% of the highly ordered dye aggregate were transformed into dye monomers after only 16 hours in darkness at high temperature and high humidity.

However, this equilibrium is fully reversible by decreasing either the temperature or the humidity or both. In the absence of light, only 2% irreversible dye oxidation was detected after 168 hours at 91°C/90% rel. humidity (R.H.). In the *presence of actinic light*, the irreversible oxidation of the dye monomer was increased by a factor of more than 100 under these adverse environmental conditions. This scheme shows that deaggregation must precede irreversible dye destruction, and this was shown to be the case for all mechanisms discussed above. These results also explain the influence of high temperature/high humidity environment on light-fastness (and even on storage in darkness) of ink-jet prints. It should be mentioned here that the absorption maxima of the aggregated state depend on the molecular geometry of the dye. In this case, the aggregated state is at longer wavelengths than the monomers, which corresponds to a geometrical arrangement like the one given in this scheme (brickstone model, dye transition moment parallel to the long axis of the chromophore schematized by rectangles).

In the case of **triplet-sensitized, photocatalytic oxidation,** deaggregation of dyes is still more important, as it enhances not only the photooxiation of the catalytically destroyed dye, but also the quantum yield of triplet formation for the sensitizing partner. Therefore, the contribution of dye deaggregation is even higher than for a single dye ("photocatalysis"). The presence of strongly deaggregating compounds in inks or in receiving layers should be avoided for light-fast ink-jet systems.

Conclusions

Our studies did not allow to forecast by which mechanism a given dye is destroyed photolytically. The fact that, in the same receiving layers, three different mechanisms of dye destruction could be found shows the complexity of light-fastness problems. Therefore, we cannot expect to find an optimum solution for enhanced light stability with all kinds of ink-jet dyes and all media, but will have to be satisfied with the best compromise. However, dye aggregation has shown to be important for all studied mechanisms, and seems to be a very important parameter for light-fastness.

Although measurements in dye solutions using a photoreactor of the type discussed are most useful as a complementary technique to understand such phenomena, results obtained do not parallel *quantitatively* those observed in ink-jet prints containing the same dye. This shows how important the chemical composition of media is for dye photolysis. Diffusion-controlled processes are different in coated layers and in solution, as well as the exchange of environmental gases (e.g. oxygen). Moreover, the extent of dye aggregation is not the same in solution as in coated layers. Therefore, we could never ***quantitatively*** extrapolate photolytic measurements in solutions to printed, coated layers. The most important conclusions concerning the ***mechanisms*** of irreversible dye destruction mentioned in this report were obtained from lightfastness measurements in **prints**, while the most relevant information concerning the influence of dye ***aggregation*** was obtained from **solution spectra**. Both types of measurements are necessary to get an overall understanding of lightfastness.

References

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Biography

Rolf Steiger received his Ph.D. in Physical Chemistry from the University of Neuchâtel (Switzerland), and was a postdoctoral fellow at the LAWRENCE Berkeley Laboratory in 1967/68. He then joined the Central Research Labs of CIBA-Geigy working on the surface chemistry of silver halides, and the ILFORD research labs in 1982. His current interests are in ink-jet media, surface chemistry and photochemistry. He teaches Surface Chemistry and Molecular Engineering as an Associate Professor at the University of Neuchâtel.