Influence of Dye Structure on Permanence

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Abstract

The light fastness behavior of several classes of colorants was investigated on different ink-jet media. Their sensitivity to ink dilution and to environmental humidity is demonstrated. Cross-coupling effects are found for certain combinations of colorants. Most observations can be explained by a dye-aggregation mechanism that is more or less affected by the experimental parameters. A specific layer design is shown to improve light stability for certain dyes.

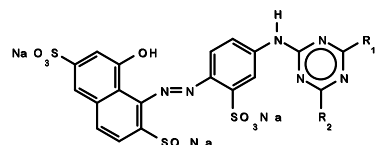
Introduction

Ink-jet printing is the hardcopy technology that achieves photo-like image quality at very moderate equipment costs. The real break-through in replacing photography on a wider scale necessitates progress in two areas, better print permanence and higher productivity. Higher productivity is expected through the use of faster absorbing media, based on capillary absorption instead of polymer swelling. However, many prints on so-called nanoporous media exhibit appreciably lower permanence than those on swelling polymer systems specifically optimized for light stability.

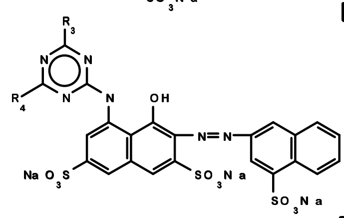
A visible gain in ink-jet image quality can be achieved by using diluted inks in addition to full-strength inks.[1] The detrimental effect of ink dilutions on permanence is well-known and has been described before.[2,3] The lower permanence of such prints sets a limit to the dilutions that can be recommended for photographic output. This paper investigates the effects of the receiving layer, the ink dilution and the environmental humidity on the light permanence of 3 magenta dyes and 1 cyan dye suitable for ink-jet printing. Dye aggregation is discussed as a plausible cause for reduced permanence and a media to improve stability is shown.

Method

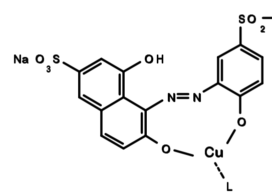
Aqueous ink formulations for a 300 dpi thermal ink-jet head were prepared with the three colorants Mag1, Mag2, Mag3 and Cyan. The three magenta colorants belong to three classes of dyes and can be characterized by the following chemical structure



Mag1



Mag2



Mag3

Cyan was a typical water soluble phtalocyanine. The full-strength inks (also called 100% ink) contain 3-5 % weight percent of colorant in an aqueous ink formulation. Diluted inks of 40%, 20% and 10% of the full strength ink were prepared by adding the ink carrier.

The printed ink-jet samples were submitted to an Atlas ci-35 weatherometer and exposed by window-glass filtered daylight at 108 klux for several days until a total exposure of 10 Mluxh was reached. The instrument was set to day/night cycles at a ratio of 3.8:1. The relative humidity during day cycles was 20%, during night cycles 80%. The black panel temperature was 60° C. This test condition is called the 'dry condition'. For the high humidity tests, the irradiance was lowered to 65 klux and the instrument ran without day/night cycles up to a total exposure of 3 Mluxh. The relative humidity during the exposure was 80%. This test condition is called 'high humidity condition'.

In the weatherometer, the samples will also experience humidity variations in addition to the exposure. The two effects are very difficult to separate in the experiment. The colorants were chosen not to show much dye diffusion up to the threshold of 80% r.h., so that dye diffusion would not mask density losses due to light.

The test images were color wedges composed of monochrome cyan, monochrome magenta and 1:1 mixtures of both for bi-chrome blue. They contained patches printed at 100%-10% ink load in steps of 10%. The printer driver and printer settings were carefully kept constant so that in the different experiments a step of the wedge corresponds to a fixed ink load.

The samples were measured before and after exposure in status A density. Density as well as percentage changes in density were reported. A typical test result for Mag2 is shown in figure 1. For the magenta wedge (top) and the blue wedge (bottom) the magenta density change is plotted as a function of the ink load (step on wedge). The four curves represent one Mag2 ink dilution each.

The density changes averaged over all ink loads were sometimes preferable as data reduction.

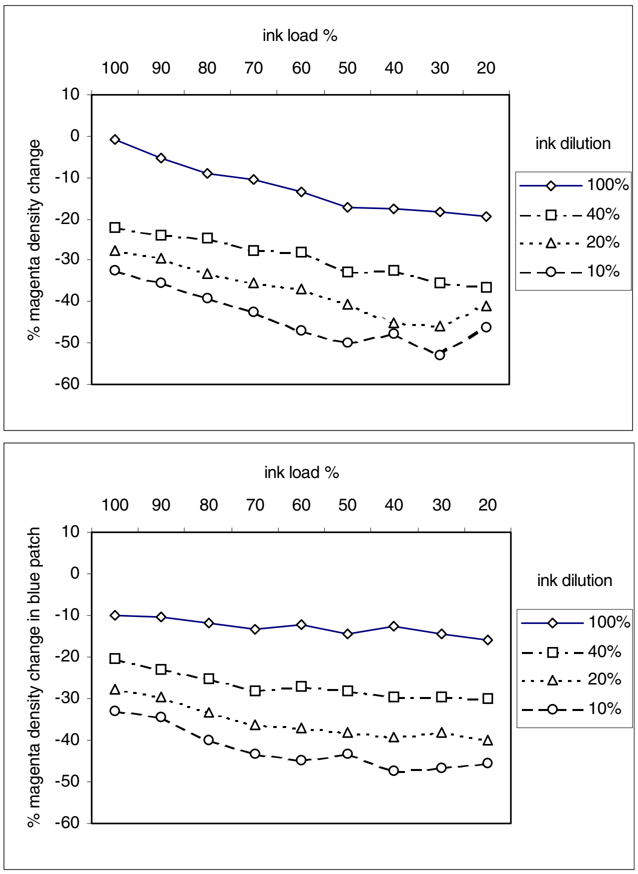


Figure 1. Typical test result for Mag2: density changes of the step wedge after 10 Mluxh exposure

Results

Influence of Substrate Type on Light Permanence

The great contribution of the receiving layer to light stability has been well established.[2] Three different commercial receiving layers were chosen in our study to show the varying effect on the three classes of dyes. One is a swelling polymer layer (DT) known for its dye stabilizing performance (ILFORD's DTPGP9 RC photo glossy paper) and the other two are microporous substrates that act by capillary absorption (Konica Photolike QP (KP) and ILFORD's Nanoporous Glossy Paper DN)). Figure 2a compares the light stability of the 3 magenta in full-strength ink on the polymer media and the microporous media KP after 10 Mluxh exposure under dry conditions. The light permanence of the three magenta is much lower on the microporous media than on the polymer layer. Figure 2b represents the light stability of a specifically optimized dye, Mag4, on two different microporous media, KP and DN, for full-strength ink as well as for a 25% dilution. With dye/media optimization, a considerable gain in light stability can be achieved and the strong dependence on dilution can be suppressed.

For our further investigation, only swelling polymer receiving layers were used.

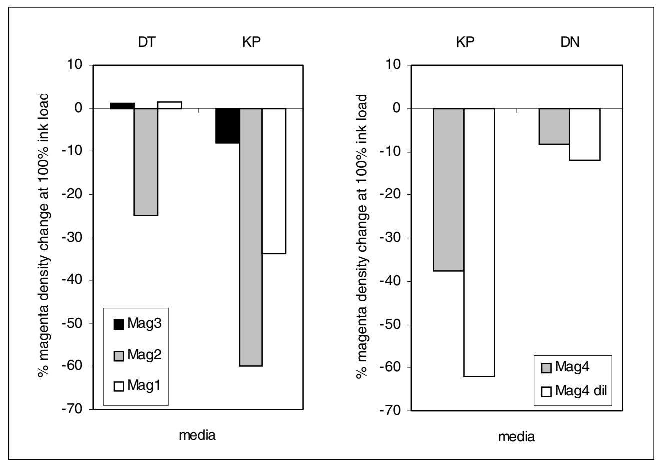


Figure 2 a,b. Light stability of magenta dyes on polymer and microporous media

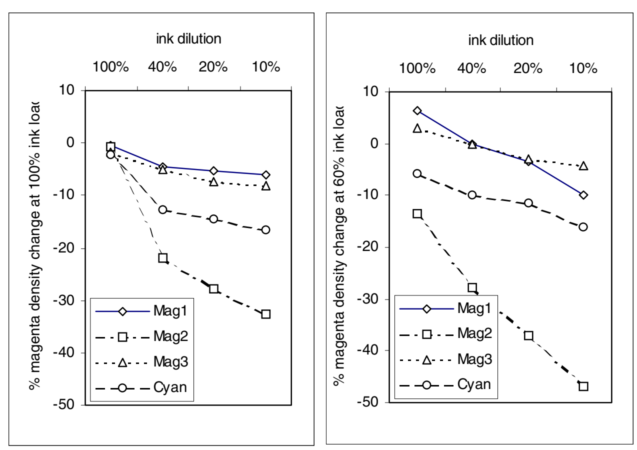


Figure 3. Density change after 10 Mluxh exposure as a function of ink dilution at an ink load of 100% (left) and 60% (right)

Influence of Ink Dilution on Light Permanence

The colorants were tested in several ink dilutions on a RC paper with a polymer layer optimized for stability (ILFOJET Professional IJP1GP7). Figure 3 shows the percentage loss of density in the monochrome wedges as a function of the 4 ink dilutions (100%, 40%, 20%, 10%). The change is shown for an ink load of 100% and of 60%.

The overall picture is similar for both ink loads. Mag3 as well as Mag1 are little affected by ink dilutions down to 10% of full-strength ink. The experimental fluctuations of the permanence tests are at least 5% for a single experiment. Mag2 shows a strong decline in light stability with dilution. Cyan exhibits a small decline of stability with dilution. Mag3 and Mag1 are azo-dyes of a class known to form stable aggregates.

Influence of Cross-coupling Effects on Light Stability

Cross-coupling effects on stability have been known for a long time in the imaging and textile industry.[5] Contrary to photography, where the imaging dyes are placed in different layers, there is no separation of the dyes in ink-jet prints. Depending on the surface coverage, the various color dots will overlap more or less. In areas of high ink load, cross-coupling effects can often be observed which are sometimes called ‘catalytic fading’. Catalytic fading becomes visible as the difference of density change of the monochrome print patch compared to the bi-chrome patch at same ink load.

In Figure 4, the difference of the change of density in the bi-chrome blue wedge minus the density change of the corresponding monochrome magenta wedge is plotted for the three magenta under dry test conditions at 100% and 60% ink loads. Whereas Mag3 and Mag2 show little variation of light permanence in the presence of cyan, Mag1 shows a decline of 10% in light fastness in the blue patch compared to the pure magenta wedge. For the three magenta tested, the catalytic fading does not vary much with ink dilution.

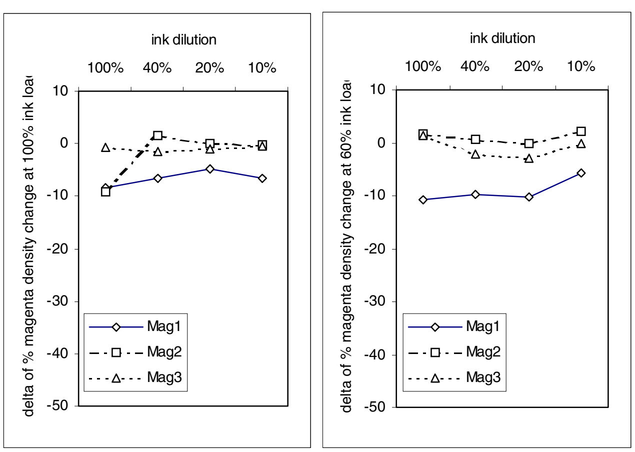


Figure 4. Catalytic fading as a function of ink dilution

Influence of Environmental Humidity

Accelerated light fading tests with high irradiance tend to dry out the test specimen, which often helps preservation. In a typical light phase of the dry condition, environmental humidity will only be 20% and the sample temperature is between 40°C to 60°C depending on the color of the patch. Such conditions will rarely be encountered in real-life fading, where the samples are cooler and more humid. The high humidity test condition (80% r.h.) was used to investigate the influence of humidity on the stability of the colorants. For figure 5 the magenta density changes were averaged over all ink loads of each of the ink dilutions. Figure 5a shows the three magenta density changes as a function of ink dilution for the dry case, figure 5b for the humid experimental condition. The differences in light stability at the two conditions are appreciable if normalized to the same total exposure of 10 Mluxh. The density changes in the humid case are typically 1.5-3 times higher than in the dry case.

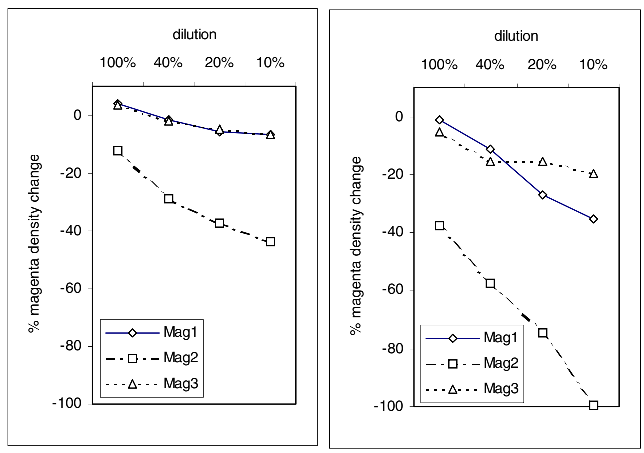


Figure 5 a,b. Magenta density changes under dry (left) and humid (right) test conditions, both normalized to 10 Mluxh

The cross-coupling effect or catalytic fading may increases as well under the impact of humidity as shown in figure 6 averaged over all ink loads per dilution. Mag2 and Mag3 are not very prone to catalytic fading and do not exhibit much additional fading under humid conditions. However, Mag1, which is more susceptible to catalytic fading under dry conditions, suffers from a strong increase in fading under humid condition. The cross-coupling effect is about three times larger in the latter case. A possible explanation is the higher dye de-aggregation of this dye under high humidity conditions.

Influence of Aggregating Media

If dye aggregation was a major factor in light permanence of ink-jet azo-dyes and phtalocyanines, media and conditions that enhance dye aggregation should improve the permanence of prints. It was shown before that very dry environmental conditions improve print permanence, but very dry conditions cannot be assumed for all locations were prints will be displayed.

The 4 colorants of this study were printed on a second swelling polymer media designed to promote dye aggregation. The results of this test are plotted in Figure 7 for the dry and humid condition. The monochrome wedges of Mag3 and Mag1 averaged over all ink loads per dilution do not show a large effect as they are not very susceptible to dye dilution (see figure 3). On the other hand, the stability of diluted Mag2 and Cyan is improved by about 10%.

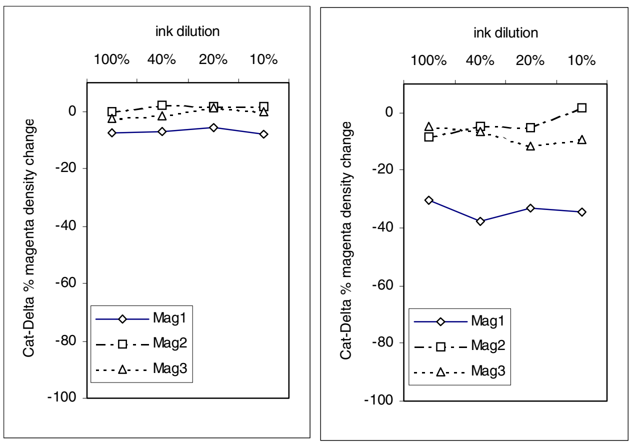


Figure 6. Catalytic fading averaged over all ink loads, dry (left) and humid (right) test conditions normalized to 10 Mluxh

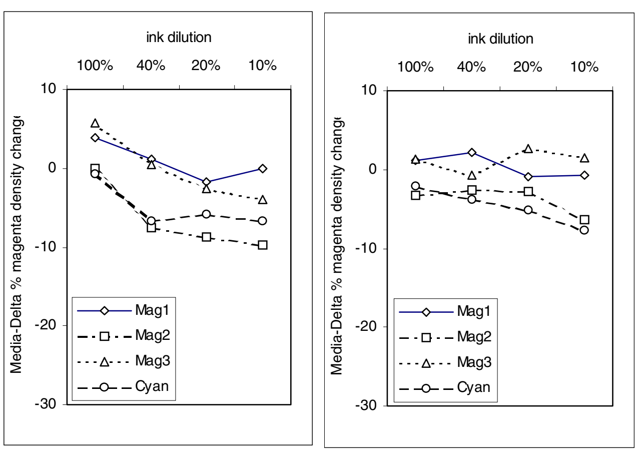


Figure 7. Influence of dye-aggregating media on light stability, dry (left) and humid (right) condition normalized to 10 Mluxh

Conclusions

The different behavior of colorants versus ink dilution could be demonstrated. The susceptibility of light fading to the ink receiving layer, to ink dilution, to humidity as well as cross-coupling effects with other colorants were investigated. A plausible explanation for many of the effects observed is dye-aggregation and complex formation of the dyes in the ink receiving layer. Conditions that lower dye aggregation such as high humidity, dilution and certain types of media can lead to a pronounced permanence loss otherwise very stable colorants. Among the classes of colorants, the susceptibility to de-aggregation may vary very much.

Cross-coupling effects of certain magenta dyes with cyan are known. They were shown to depend on the type of dye, but not on the ink dilution.

Acknowledgements

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Biography

Mario Fryberg received his PhD in organic chemistry from Simon Fraser University Vancouver, B.C. First, he worked in the area of synthetic polymers. Since 1975 he has been affiliated with Ilford Imaging in Switzerland, with his main activities in organic syntheses and the development of components for photographic applications. Since 1993 he has been in charge of Ilford's ink-jet dye and ink development program.