The Characterization of Humidity Sensitivity of Ink-jet Prints

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Abstract

Diffusion of dyes in ink-jet prints under high humidity is one of the major causes of print degradation. There is, however, no agreed method how to characterize humidity sensitivity and how to predict failure from accelerated test. The study comprises humidity degradation tests of various ink sets on polymer, porous and nanoporous IJ media. It compares different test patterns, pre-conditioning methods, test conditions, and metrics for humidity. From the extended test set, conclusion could be drawn about the media factors that are most important for humidity degradation, namely the type of colorants, the class of media or the ink vehicle. Some recommendations about test patterns and test methods are discussed.

Introduction

The life expectancy of stable prints is determined by extrapolating from accelerated ageing tests. The impact of heat, light, humidity and pollutant attack on the prints is typically investigated individually while maintaining all other environmental factors constant.¹ The overall life expectancy is extrapolated from the sum of all degradation mechanisms. This procedure assumes linear behavior between the environmental factors. However, recent publications have shown^{2, 3, 4}, that humidity can accelerate light degradation. Thermal dark reactions are very dependent on humidity, as well, as is known from photography in test above the glass temperature of gelatin. Even the rate of the reaction with environmental pollutants is known to be accelerated by humidity.

Figure 1 shows two light stability test run for one particular ink/media combination under (a) cycling light dry (40% r.h.) and dark humid conditions (80% r.h.)compared to the same test done up to the same exposure for (b) only dry (40% r.h.) conditions. The humidity sensitive magenta dye degrades much faster in the cycled test (9% faster). The graphs also shows one difficulty of running light stability test at high humidity. The degradation of dyes that tend to diffuse under high humidity (y in fig 1.) is masked by the increase in density due to higher dot gain. Unfortunately, laminating the prints only reduces the effect (figure 1c,d), as laminates have considerable water vapor permeability.



Figure 1. Relative density loss as a function of MluxH light exposure for four conditions (a) to (d)

Knowing the humidity sensitivity of prints at different humidity conditions as well as their change over time at elevated humidity is important for overall life expectancy predictions and studies of interactions of humidity with other degrading factors. The following study tries to develop test methods, test patterns and metrics to characterize humidity sensitivity.

Experimental Conditions

The humidity study was done on a large sample set including papers with polymer layers on RC base, nanoporous layers on RC base and one matt coated paper. The inks were all dye-based, thermal or piezo inks, some commercial and some experimental to test vehicle influence. Test print patterns were full pure colour (Y, M, C, K, 3K, B, G, R) cross-hatches on white or yellow background, medium density greys and line width targets. The prints were dried for at least 24, or at most 48 h before being submitted to the test unless specified otherwise. The incubation chamber was a Weiss Technik device, temperatures and humidities were varied as indicated in the individual test. Humidity diffusion was measured with a Gretag/Macbeth Spectrolino either as Status A density change on the cross-hatch pattern (5) or as Lab Delta E on the grey patches.

Results

Test Pattern Influence

A recent study on the influence of the background colour on the diffusion of coloured lines⁶ suggested that dye diffusion can be stronger against a coloured background than against a white background. The cross-hatch pattern of full colour lines was printed on a white background and a full yellow background for two commercial thermal and one piezo ink on 3 different nanoporous media based on alumina as well as silica layers and two polymer papers. The samples were kept at 40°C and either 60% r.h. or 80% r.h. for 7 days and the density change was measured. Diffusion at 60% r.h. was so small for both backgrounds that the density changes are not significantly above noise. Figure 2 shows the result of the absolute changes of the magenta patches averaged over the polymer and the porous papers separately for the test done at 80% r.h. The yellow background enhances the dye diffusion especially in the polymer papers, but less in porous papers. The ranking of the ink/paper combinations was maintained. The results of the cross-hatch pattern on white were further correlated to the changes in medium density greys. The diffusion of full colour cross-hatch pattern correspond to a line width spread and does not correlate well with the colour change in light grey, which measures single dot gain. Both properties need separate test patterns and investigation.



Figure 2. Absolute density changes of a magenta crosshatch pattern on white or yellow background at 80% r.h. and for two media types

Ink/Media Influence

There has been considerable discussion about the right metrics for humidity diffusion. The point of relative humidity at the onset of significant diffusion could be taken as a criteria as well as the extent of diffusion. Means over many colours as well as maximum single colour changes could be used.

Figure 3 illustrates the humidity behavior of typical ink-jet prints on polymer RC paper, nanoporous RC paper and one matt pigment coated paper exposed to 7 days at 50%, 60%, 70% and 80% r.h. to investigate their threshold behavior. Shown are the average of the density changes at different humidities for one ink on different media of all colours (a), for the yellow and cyan patch (b, c) only and the change at 80% r.h. for all inks on all media. Most prints have very little humidity diffusion at or below 60% r.h. and show a more or less steep increase between 70% r.h. and 80% r.h. Humid fastness is influenced by the media matrix as well as by the ink. Media 3 in fig 3d exhibits on average significantly higher diffusion than media 4 for example with all inks. Ink 2 tends to diffuse less than ink 1 and 3. But there are very specific interactions as well, like the ink 1 yellow on media 4 in fig 3b.



Figure 3. Relative density changes in % at different humidities (% r.h.) for all colours (a), cyan (b) and yellow (c). All inks and media in part (d) at high humidity

While most colours diffused independent of each other, we found some examples of enhanced diffusion in bichromic colours as shown in fig 4 for a magenta in pure magenta and in the red patch for a polymer (a) as well as a porous (b) matrix. In the case of the porous matrix, the point of first significant diffusion shifts with a second colour present, in the case of polymers it does not, but the second ink influences the strength of the diffusion.



Figure 4. Enhanced diffusion for a magenta patch depending on media type



Figure 5a. Relative change in density without and with preconditioning. Inkset 1.

The slope of this increase or the point of onset of the slope could be ways to measure humidity fastness. On the other hand, as the crossing curves of fig 3 a and b illustrate, the high humidity data are not necessarily representative of the behavior of the media at low humidity.

Influence of Sample Conditioning

From light stability studies⁷ it is known that the pretreatment of samples can have a profound effect on the result of a permanence test. The drying time before the test acts in at least two ways, it may remove humefactants and solvents more thoroughly than short drying and it suppresses the short term color shift often seen on freshly printed materials. A third set of experiments was targeted at finding the right pre-conditioning. Two ink sets were printed on 3 different nanoporous media (2 alumina, 1 silica) and two polymer media. Samples were either preconditioned or normally dried for 24h at 50% r.h. before they were put into the humidity chamber. They were kept at the specified humidity for 35 days, with measurements taken every 7 days.

Figures 5 a and b show the results of these tests. Plotted is the colour with the maximum change in density on the cross- hatch pattern. The samples at 60% r.h. did not show significant dye diffusion. Ink 1 showed change after 35 days at 70%. However, all samples printed with ink 2 showed well above 10 % change as the maximum deviation.



Figure 5b. Relative change in density without and with preconditioning. Inkset 2.

Three different pre-conditioning methods were tried, one day forced drying at 60°C in an oven, 12 hours or 7 days drying at very low humidity in an exsiccator. The specially treated samples were later submitted to 80% r.h for 35 days at 14°C. None of these pre-conditioning methods produced significantly different results from the usual ambient drying.

Conclusion

Several material factors are responsible for dye diffusion in prints, the two most important ones are the media matrix and the dye.

For the ranking of the diffusion sensitivity of media and ink, it is important that the test pattern contains full colour lines adjacent to lower density lines, so that the line spread on high density can be measured. Line spread against white background is probably representative for line spread in general concerning ranking. Monochrome as well as bi-chrome composite black need to be present as there may be enhanced diffusion on composite colours. Colour shift on light colours, especially in grey, upon the impact of humidity is an different criteria that should be measured independently.

Most of the water present from printing is evaporated after 24h in a normally vented room at ambient condition. Forced drying test did not reveal a change in dye diffusion compared to simple drying.

There has been disagreement about the right metrics to qualify humidity sensitivity. Due to the complexity of the ink/media interactions, it is probably not easy to come up with one metric for humidity fastness. The change of density after a specific time at elevated humidity provides one way of ranking. A different ranking would result if the evaluation was based on the humidity at which a certain threshold change was reached. Yet another ranking if the change of colour was followed at one humidity as a function of time. The full characterization of media may require all three tests to be performed.

The ranking of the performance of inks, dyes and media is only the first step to the actual question of interest which is the life expectancy of a print kept at a certain humidity or uncontrolled humidity in the dark. For prints with very low humidity fastness or for high humidity, humidity diffusion can be investigated in real-time. For very stable prints or prints kept at low humidity, the real-time test would take very long. However, accelerated test are difficult to design. Moderate temperatures are not known to speed up humidity diffusion considerably. Raising the humidity level is not a suitable procedure, as the performance at higher humidity does not represent the behavior at lower humidity well.

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Biography

E. Baumann studied physics at Fribourg University. Since 1968 he has worked with Ilford in the area of photographic sensitometry, color science and image quality and has published several papers in this field. Since 1985 he has been active in digital imaging, first for digital photography later in ink-jet with a focus on colour science and test methods.