A Closer Look at the Effects of Temperature and Humidity on Inkjet Photographic Prints

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Abstract

Previous attempts to measure the thermal dark fade of inkjet prints by the Arrhenius method have been confounded by dye migration. When tests are carried out at a constant, absolute humidity equivalent to 50% relative humidity (RH) at 24°C (constant 13°C dew point), temperatures as high as 75°C can be utilized for many ink-media combinations without encountering significant dye migration. Concerns have been raised that these conditions might result in much lower levels of residual moisture in the image-bearing layers, and this in turn might affect the observed rates of density loss and/or yellow stain formation. In this paper, we compare the results for Arrhenius studies of inkjet photographic papers and inks that have been run under both constant 13°C dew point and constant 50% RH conditions. We also explore the interrelationship between temperature, dew point, and relative humidity over narrower ranges that might be found in an indoor home environment.

Introduction

In previous reports, we have discussed various aspects of light fade and humidity keep of inkjet prints made with different types of inks and papers.[1–4] The high sensitivity of certain combinations of ink and paper to ozone has also been reported.[5–7] For prints intended for indoor display in a home or office, there is a need to estimate useful print life with respect to all relevant environmental factors, including light, heat, humidity, and air pollutants such as ozone. With respect to the effects of heat on dye stability, accelerated testing using an adaptation of methodology first described by Arrhenius[8] over a century ago has been used for traditional silver halide photographic materials.[9-11] This method is based on the relationship between the rate of a thermally activated process and temperature, as represented in the following equation:

$$\ln (k) = -(E_a/R)(1/T) + \ln (A) \quad (1)$$

where k is the rate of the process, E_a is the activation energy of the process, R is the universal gas constant, T is the temperature in the Kelvin scale (K), and A is a pre-exponential factor.

For processes that are too slow to measure practically at ambient temperature, e.g., the fade in photographic prints, the rate can be increased to more experimentally accessible scales at elevated temperatures. Equation 1 can then be used to calculate the rate of dye fade at other temperatures, thus allowing the estimation of the time it will take to reach a given level of fade or change at room temperature.

Although the Arrhenius methodology works well for simple thermally activated phenomena, it can be difficult to interpret when either more than one rate constant is involved or the system being studied undergoes a phase transition.[12] An example of the latter might be found when a dye is absorbed in a polymer matrix that has a glass transition temperature, T_g, not far above ambient temperature. A further complication occurs when the T_g of the polymer matrix is also found to be a sensitive function of absorbed moisture, which might occur in response to changes in atmospheric humidity. In previous studies of thermal fade of inkjet prints, we found that by testing under constant absolute humidity (constant dew point) conditions, temperatures as high as 75°C could be employed without evidence of significant dye migration.[13,14]

Concerns have been raised that these conditions might result in much lower levels of residual moisture in the image-bearing layers, and this in turn might affect the observed rates of density loss and/or yellow stain formation. In this paper, we compare the results for Arrhenius studies of inkjet photographic papers and inks that have been run under both constant 13°C dew point and constant 50% RH conditions. We also explore the interrelationship between temperature, dew point, and relative humidity over narrower ranges that might be found in an indoor home environment.

Materials and Methods

A list of the different glossy photographic quality inkjet media included in this study is given in Table 1. The printers/inks used for this study are listed in Table 2. All printers were equipped with current generation OEM-branded print heads and inks. Not all combinations of ink and media were studied under all conditions. The test targets and methods used in this study have been described previously.[1,13,14]

Table 1: Glossy Inkjet Media Used in this Study

Brand	Description	Type*
HP	Premium Plus (Q1785A)	S
Epson	Premium (SO41667)	P
Canon	Photo Paper Pro (PR-101)	P
Fuji	Premium Plus (7410144104)	S
Fuji	Gallery Select (7410140133)	S
Ilford	Printasia (199 9488)	P
Konica	Professional Weight (LBED4PA)	P
Kodak	KODAK Professional Inkjet Paper (bulk production)	P
Kodak	KODAK Ultima Picture Paper (bulk production)	S

*S = swellable; P = porous

Table 2: Printers and Inks Used in this Study

Model	Ink Cartridges	Type*
HP 8450	HP97/HP99	D
HP 5740	HP96/HP97	D
Epson R300	T048XXX	D
Epson 2200	T034XXX	P
Epson R800	T054XXX	P
Canon i950	BCI-6X	D

*D = dye; P = pigment

Table 3: Temperatures, Humidities, and Dew Points

Temperature (°C)	RH (%)	Dew Point (°C)
24.0	50.0	13.0
35.0	26.5	13.0
45.0	15.5	13.0
55.0	9.4	13.0
65.0	5.9	13.0
75.0	3.9	13.0
25.0	50.0	13.9
35.0	50.0	23.1
45.0	50.0	32.2
55.0	50.0	41.2
65.0	50.0	50.3
75.0	50.0	59.3
20.0	20.0	-3.4
20.0	50.0	9.3
20.0	60.0	12.1
20.0	70.0	14.4
20.0	80.0	16.5
20.0	90.0	18.3
30.0	20.0	4.7
30.0	50.0	18.5
30.0	60.0	21.4
30.0	70.0	23.9
30.0	80.0	26.2
30.0	90.0	28.2

For the Arrhenius study, samples were treated under two separate sets of humidity conditions: (a) constant 13°C dew point, and (b) constant 50% RH. The temperatures used for this study were 35, 45, 55, 65, and 75°C. In addition, a separate set of samples was kept in a dark, ozone-free chamber at 24°C, 50% RH, 13°C dew point. For the humidity keep experiments, samples were treated at 20, 50, 60, 70, 80 and 90% RH at both 20°C and 30°C. Table 3 summarizes these conditions.

For the Arrhenius studies samples have been monitored at various time intervals at each temperature up to 112 days at this point; tests are ongoing. For the humidity keep studies samples were monitored at 7, 14, 28, 56, 112, and 180 days. A Gretag-Macbeth Spectrolino was used to monitor Status A density and CIELab colorimetry. All changes to the color patches are relative to an initial starting density of 1.0 with ½ D-min correction. D-min measurements are averaged from two separate areas per sample.

Results and Discussion

Effect of Humidity on Arrhenius Testing

We saw no evidence of humidity-induced dye migration over the temperature range covered in this study when the dew point was held constant at 13°C; however, significant dye migration, as measured by density gain, was observed at temperatures as low as 45°C at 50% RH (Figure 1). Insufficient fade has been observed at the constant dew point condition to construct an Arrhenius plot at this point for the ink-media combinations included in this study. These results are consistent with our previous Arrhenius studies on dye-based inkjet systems.[13,14]

Conversely, we saw unusual density gain as a function of temperature at constant 13°C dew point for the yellow pigmented inks in combination with several of the porous media (Figure 2). Much less change was observed for these same inks at constant 50% RH. The effect is noticeably worse on certain porous media than on others. No significant changes or trends were observed for the other pigmented inks under either set of conditions on any of the media.

This unusual thermal behavior for yellow pigmented inks was first noted in our previous study.[14] Clearly this raises concerns about the long-term thermal stability for this class of pigmented inkjet prints. Given the non-Arrhenius behavior of this phenomenon, it is unclear how or if these changes will manifest themselves over longer periods under typical ambient conditions. Further work is underway to better understand the nature of this phenomenon.

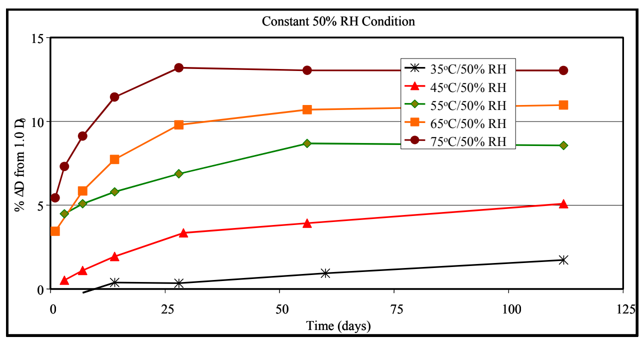

Figure 1. Percent change in density as a function of time and temperature for the yellow ink of System A (OEM matched dye-swellable system) at constant 50% RH.

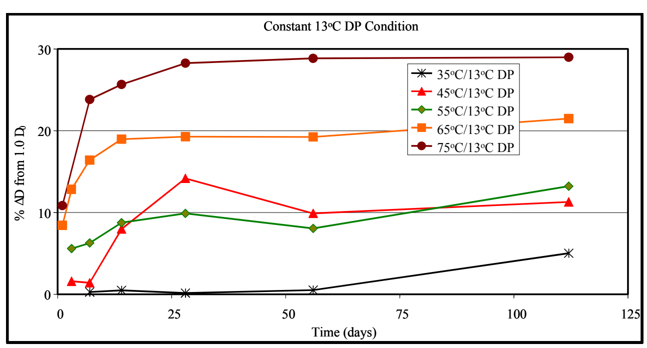

Figure 2. Percent change in density as a function of time and temperature for the yellow ink of System D (OEM matched pigment-porous system) at constant 13°C dew point.

In addition to density changes in the inked areas, long-term thermal keeping is known to also result in noticeable staining of the D-min areas of the media.[14] This is typically observed as an increase in the blue density over time, causing the media to take on a yellowish cast. All of the media included in this study exhibit some level of D-min yellowing under either constant RH or constant dew point Arrhenius conditions. An interesting observation is that all of the porous media exhibit a greater tendency to yellow under the constant 13°C dew point condition, while all of the swellable media yellow faster at the constant 50% RH condition.

Figures 3 and 4 show the Arrhenius plots for the worst examples in each class. For the porous example, sufficient yellowing has occurred at even the lowest temperature-humidity conditions to allow those temperatures to be included in the Arrhenius plots. It can be seen in Figure 3 that although the slopes of the Arrhenius equations for each condition are different, they in fact converge at the lower, near-ambient temperatures. For the swellable example shown in Figure 4, the rates of yellowing are in general much slower, and only temperatures from 45°C to 75°C can be plotted with reasonable confidence at this time. In this case, the convergence is not as obvious. Additional time at the lower temperatures will be required to understand whether the differences in moisture content of the swellable media results in non-Arrhenius behavior.

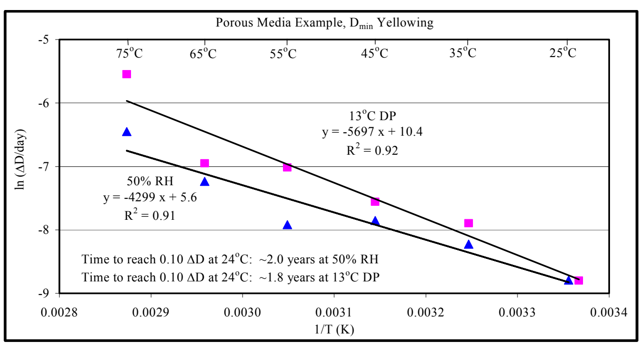

Figure 3. Arrhenius plots for the increase in D-min blue density (yellow stain formation) for a worst-case porous paper under both conditions.

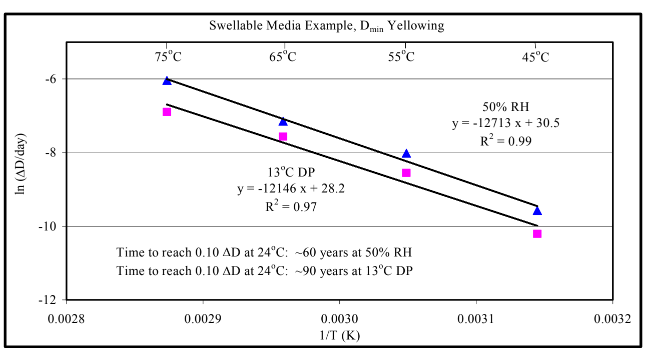

Figure 4. Arrhenius plots for the increase in D-min blue density (yellow stain formation) for a worst-case swellable paper under both condtions.

An important conclusion is that the Arrhenius equation derived for both approaches – either constant RH or constant dew point – should converge at the same common ambient condition, i.e., 24°C, 50% RH, and 13°C dew point in the case of the present study. The effect of moisture content of the media might affect the slope of the Arrhenius plot, but not the extrapolation to the ambient condition, unless a phase change or other competing degradation process results in non-Arrhenius behavior over the temperature range of interest.

Effect of Humidity at Temperatures Near Ambient

The effect of humidity at temperatures near ambient on inkjet prints is considerably more complicated than the effect of the other environmental factors. High humidity is causes dye migration, which can be observed as an apparent increase in density, often accompanied by a noticeable loss in perceived sharpness.[4,15-19] For some systems, high humidity can also lead to dye fade, especially for dyes that are susceptible to hydrolysis. For temperatures in the 20–30°C range, most systems are quite stable at relative humidities below about 60%, in the absence of light and ozone. High humidity has also been shown to accelerate the fade caused by light and ozone for some systems.[7,18]

To accelerate the effects of humidity on inkjet prints, some studies have utilized combinations of elevated temperature and humidity as high as 40°C, 85% RH, 37°C dew point.[16] However, there is a concern that such an extreme combination of high temperature and humidity may be confounding, especially for dyes that may be prone to both migration and hydrolysis. Recent evidence suggests that there may indeed be competition between dye migration and dye fade for studies carried out at 38°C, 80% RH, 34°C dew point.[20] In order to better understand and isolate the effect of humidity from temperature, we have explored in more detail the effect of varying humidity at temperatures in the 20–30°C range.

For the vast majority of the dye-based ink-media combinations included in this study, plots of density change vs time at elevated humidities display what appears to be first order, diffusion-controlled dye migration that reaches a plateau between 56 and 112 days. The behavior is qualitatively similar to that observed for the Arrhenius study at constant 50% RH shown in Figure 1. Figure 5 shows the effect of humidity at constant 20°C for the same dye-swellable system as shown in Figure 1. Figure 6 shows the effect of humidity at 20°C at 112 days for the individual primary colors for a 3-ink system. The mixed neutral for this system displays almost identical behavior, suggesting that very little dye-dye interaction is occurring in response to varying humidity. However, for this same ink set on other swellable media, much less density gain is observed for the dyes in a mixed neutral than for the pure primaries.

The onset of dye migration, as evidenced by density gain, as a function of humidity, varies as a function of dye class and media type, but typically occurs near 60% RH for dye-swellable combinations. In general, the Epson and Canon dye-based inks included in this study displayed less humidity sensitivity than the HP inks when compared on a common swellable medium. The Epson pigmented inks showed the least humidity sensitivity; however, the yellow ink does show a slight increase in density at the higher humidities after 112 days of incubation. It is unclear if this observation is related to the density gain noted above for this same ink in the constant dew point Arrhenius study. Another general observation is that the porous media exhibited less density gains with dye-based inks than swellable media in the 60–80% RH range; however, all media exhibited severe dye migration and loss of sharpness at the 20°C, 90% RH condition. This was not observed for the pigmented inks.

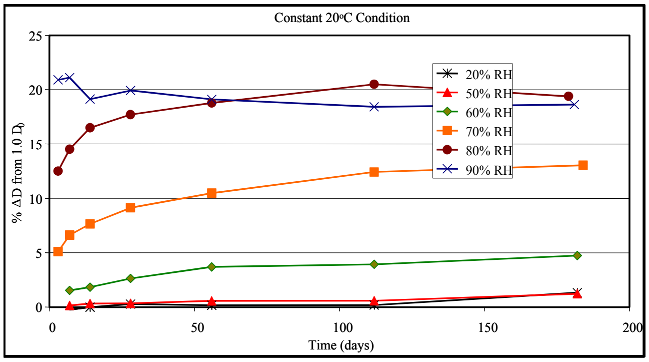

Figure 5. Percent change in density as a function of time and relative humidity for the yellow ink of System A (OEM matched dye-swellable system) at constant 20°C.

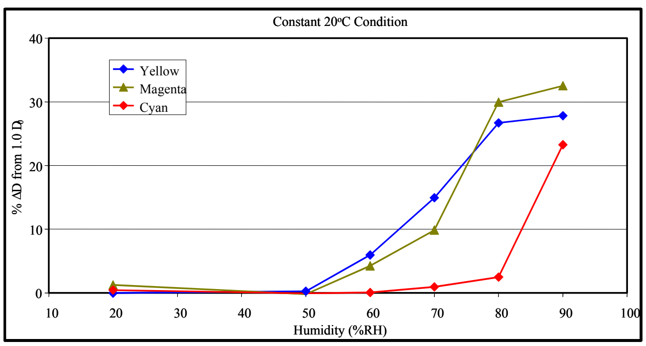

Figure 6. Percent change in density as a function of relative humidity for the CMY ink set of System B (OEM matched dye-swellable system) after 112 days at 20°C.

The effect of RH at constant 20°C on D-min yellowing seems to parallel observations from the Arrhenius studies. The porous media exhibit a greater propensity to yellow at the lower humidities, especially at 20% RH, while the swellable media yellow to a lesser degree only at humidities in the 80–90% range. It is unclear at this time why porous and swellable media display this opposing behavior as a function of humidity.

By comparing the results of the Arrhenius studies and the humidity keep study, it is clear that neither relative humidity nor absolute humidity (dew point) alone can explain the observed phenomena. For example, as the temperature is raised at constant 50% RH, density gain is observed (Figure 1). On the other hand, as the temperature is lowered to 20°C at a dew point of 13°C, which occurs between 60 and 70% RH, density gain is also observed (Figure 5). Furthermore, severe image smear is observed at a dew point of only 18.3°C at a temperature of 20°C, but much less dye migration and very little image smear are observed at dew points in the 30–60°C range covered in the Arrhenius study at constant RH. The likely explanation is that the moisture content of the image-bearing coating is a function of both temperature and humidity, and it is the moisture content in the vicinity of the dye that triggers dye migration resulting in density gain and eventually loss of sharpness.[21]

Conclusions

Arrhenius studies of dye fade for inkjet systems are complicated by dye migration when studies are carried out at a constant 50% RH condition. However, by using a constant dew point approach, temperatures up to 75°C have been achieved. For pigmented inkjet systems non-Arrhenius behavior is observed for certain yellow pigments under the constant dew point condition. On the other hand, Arrhenius studies of D-min yellowing were successfully carried out under both conditions. For well-behaved media, the Arrhenius equations under each condition were found to converge at an ambient environment of 24°C, 50% RH, 13°C dew point.

This study confirms that the effect of heat on the image stability of inkjet photographic materials can be isolated from the other known environmental factors: light, humidity, and air pollutants, such as ozone. Based on the results of the present study, it appears that the long-term effects of heat cannot be summarily dismissed as insignificant. Given the clear influence of both the ink and media on this phenomenon, it is imperative that any testing intended to produce a realistic print-life claim must include some form of Arrhenius or other thermal fade testing in order to substantiate whether heat is or is not a significant environmental factor.

The effect of humidity at temperatures near ambient on inkjet prints is considerably more complicated. Dye-swellable combinations are sensitive to relative humidities above about 60% RH, which appear to trigger dye migration resulting in observable density gain and eventual loss of sharpness. Dye-porous combinations are less sensitive below 90% RH, but they also exhibit severe dye migration at very high humidities. Pigmented inks are generally insensitive to elevated humidities. Humidity was also observed to result in D-min yellowing, which appears to parallel the observations from the Arrhenius studies. In this case, lower humidities produced objectionable D-min yellowing on one of the porous inkjet papers included in this study.

Acknowledgments

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Author Biography

Douglas Bugner received a BS in Chemistry from The Ohio State University (1975), an MS in Organic Chemistry from UCLA (1980), and a PhD in Organic Chemistry from UCLA (1982). Dr. Bugner joined Eastman Kodak Company in 1982, and in 1993 he established a research effort in the area of inkjet materials. The Inkjet Materials Technology Laboratory was formed in 1994, which he headed until 1999. He is currently Senior Laboratory Head, Cut-Sheet Media Commercialization Lab, Inkjet Systems Program. He holds 58 U.S. Patents, and has authored over 40 scientific publications.