Journal of Imaging Science and Technology® 53(4): 040501–040501-6, 2009.

Semiempirical Predictive Kinetic Model of Light Induced Magenta Dye-Based Ink Jet Ink Fading on Polymer-Coated Photomedia

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Abstract. *With the dramatic increase in the prevalence of photoprinting using ink jet printers in recent years, much effort has been made to increase the longevity of the resulting prints. Many of these phenomena, unfortunately, require long-term testing in order conduct an accurate assessment. Much of the testing to date has been purely empirical in nature, allowing little improvement from a rational perspective. To overcome these limitations, this paper introduces a simple model of the light induced fading of magenta dye-based inks on polymer-coated photo media that represents fading as a two step process. Using this model, fade data collected in as little as nine days may provide accurate predictions of these ink/media combinations out to approximately 20 years of simulated fading. In many instances, the model can be further simplified. This analysis allows the definition of a "light fade factor" for both the ink and media which may serve as a useful figure of merit to facilitate the rapid qualitative comparison of ink and media formulations.*

[DOI: 10.2352/J.ImagingSci.Technol.2009.53.4.040501]

INTRODUCTION

Recent improvements in the rendering of photographic images by ink jet printers have been dramatic.[1] This improved image generation has enabled consumers to create their own hard copy photographs that often rival the quality of traditional photographic prints. Unfortunately, this new ability has not been realized without problems. One of the most profound shortcomings, which has received a considerable amount of research attention, is the permanence of the prints generated by ink jet printers.[1] While silver halide prints have historically exhibited lightfastness up to 60 years, early ink jet prints often faded to unacceptable levels in less than ten years.[1–5]

Recent developments in ink jet technology have done much to address this shortcoming, but the results have been mixed. Several failure modes for printed images generated with dye-based inks have been identified, including light induced fading, ozone induced fading, and degradation in humid or dark storage.[6–8] While certain combinations of ink and media have been shown to exhibit in excess of 100 years of archivability in accelerated testing, the choice of ink and media are of paramount importance. The same ink on a different photo medium may exhibit significantly less permanence. Therefore, any ink/media combinations under consideration must be tested.[3,4,9] In addition, it is typically necessary to evaluate numerous potential failure modes, including lightfastness, dark-fastness, humidity-fastness, and ozone-fastness.[10–13] This accelerated testing typically relies on the underlying assumption that the law of reciprocity is obeyed.[14–17]

The typical test for lightfastness involves the use of accelerated fading by exposure to high intensity light sources.[8,18–20] While the acceleration factor of these tests may be between 150–700, it is often necessary to fade samples for several months in order to assess long-term stability.[8] It would be useful, then, to have a model that would accurately predict the fading of inks in a shorter period. Such a model would allow for meaningful comparisons between ink and media systems to be obtained in as little as one month even for systems that exhibit exceptional lightfastness and would facilitate the rapid development of improved ink systems.

This paper describes the use of a technique often employed in the modeling of catalytic chemical reactions in order to develop such a model.[21–23] Since different dyes can exhibit vastly different permanence properties, this initial study was conducted using dye-based inks in order to develop a technique that can model a wide range of behavior. By making several assumptions about the system under consideration, it is possible to construct a model using two parameters that describes the fading of a specific ink-medium combination and that can be used to predict future fade behavior accurately. In many instances, this model can be further simplified and can be accurately defined by one parameter.

EXPERIMENTAL

Ink Formulation

Each ink was a typical aqueous ink jet formulation containing with 3% (wt./vol) dye, 8% 2-pyrolidinone, 6% tetraethyleneglycol, 6% tripropylene glycol, 3% 1,2-hexanediol, and 0.5% Silwet L-7600.[24] Five dyes, shown to exhibit a wide range of permanence, were employed in this

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Received Nov. 23, 2008; accepted for publication Mar. 3, 2009; published online Jun. 4, 2009.
1062-3701/2009/53(4)/040501/6/$20.00.

Table I. Summary of dyes used in ink formulations.

Dye	Description	Lightfastness	Light fade factor
D1	Lexmark magenta dye	Moderate	2.48
D2	Ilford magenta dye	Good	3.91
D3	Metallized magenta azo-dye	Excellent	5.14
D4	Sensient acid red 289	Moderate	1.37
D5	Sensient acid red 52	Poor	7.50×10^{-7}

Table II. Summary of media used in fade experiments.

Media	Description	Lightfastness	Light fade factor
M1	Kodak premium photo paper Glossy	Moderate	3.23
M2	Ilford printasia photo glossy paper	Excellent	4.30

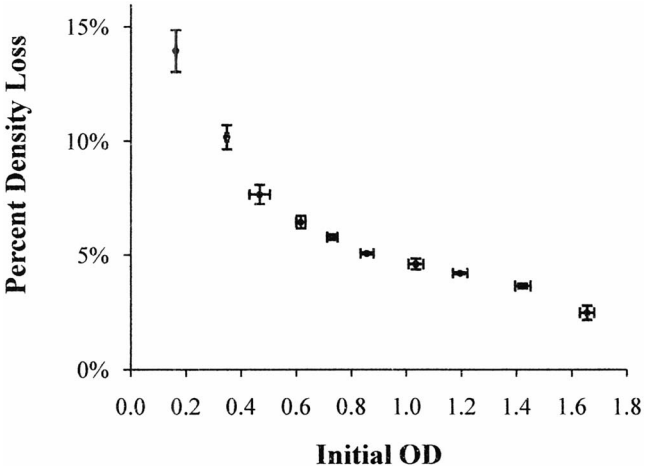

Figure 1. Observed fade after 720 h of exposure: ink D2, media M2. Error bars represent ±1 standard deviation.

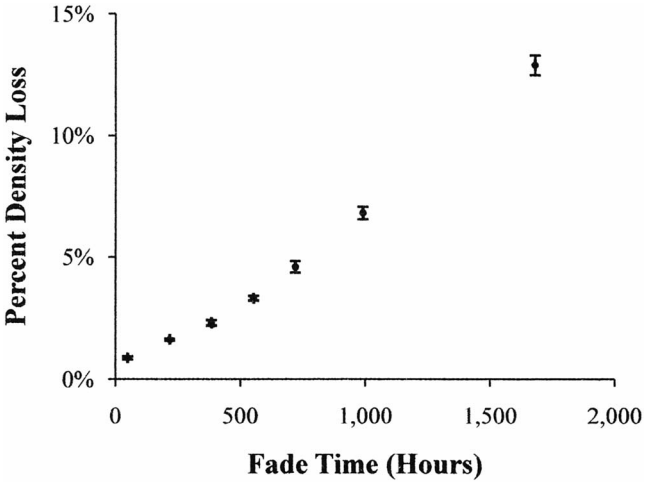

Figure 2. Observed fade as a function of time: dye D2, media M2, initial OD 1.03±0.03. Error bars represent ±1 standard deviation.

study and are summarized in Table I. Acceptable performance of these inks was verified in print cartridges prior to printing the samples for fading.

Sample Preparation

In order to develop a model with broad applicability, the five inks were each tested on two glossy polymer-coated photo media. As indicated in Table II, images printed on these two media typically exhibit differing degrees of light stability. Samples for light fastness testing were generated using a Lexmark z65 ink jet printer. For each color, a minimum of ten patches of varying density was printed with each ink/medium combination using a specially coded print driver that allowed precise control over density of ink droplets on the media. Additionally, three independent sets of samples were generated for each ink/medium combination. The optical density (OD) of the patches used in this work varied from 0.25 to 1.7. These samples were allowed to dry at 70°F and 50% relative humidity for 14 days before fading.

Measurements

Prior to exposure to the fluorescent radiation, the color and optical density of each colorant patch was measured using a Gretag Spectrolino/Spectrascan with D50 illuminant, 10° observer angle, and ANSI status A density standard. Periodically, the samples were removed from the fade apparatus, additional color and density readings were obtained, and the samples were returned to their original positions in the fade apparatus.

Light Fade

After drying for two weeks, the samples were faded in a specially designed apparatus modeled after the fluorescent fade units employed at Rochester Institute of Technology's Image Permanence Institute.[14] The samples were mounted in aluminum samples holders and placed in the unit behind a glass filter with an air gap of approximately 3 mm. Triplicate sets of samples were placed randomly throughout the fade apparatus to minimize the effect of positional bias. The samples were maintained at a constant temperature of approximately 70°F and relative humidity of 50% and were exposed to cool white fluorescent radiation at approximately 40 kLx. They were typically allowed to fade until either 50% density loss was observed in the samples or until ten weeks of accelerated testing had occurred. While no attempt was made to control the level of atmospheric ozone, previous in house studies with these ink/media combinations confirm that the contribution of ozone induced fading is negligible in the time frame of these experiments.

RESULTS AND DISCUSSION

For each data point, the fade is represented by the percent density loss which can easily be calculated based on the initial and observed optical densities of the colored patches using Equation (1).[25] As can be seen in Figures 1 and 2, which are typical of the observed fading behavior, the percent density loss for a given ink-media system is a function of both the initial optical density of the patch and of the

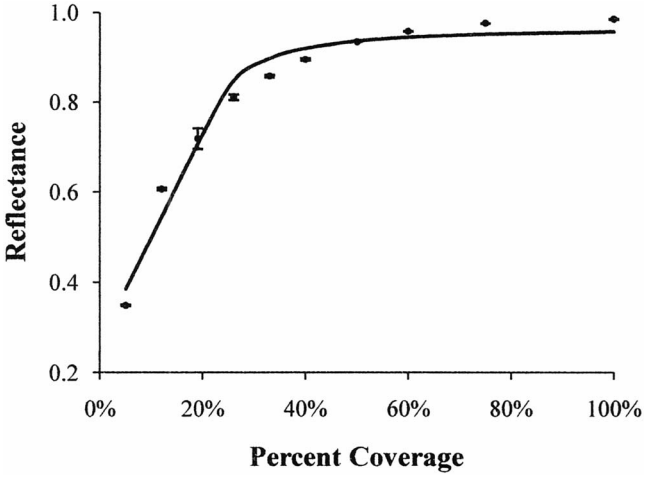

Figure 3. Relationship between surface coverage and reflectance. Data points represent experimental measurements, while the curve represents values predicted by the model. Error bars represent ±1 standard deviation. Ink D1, media M1, a=0.677, and b=0.293.

exposure time. In order to develop a model, then, both of these variables must be included. Attempts to develop a comprehensive model based on the value of the OD and on the exposure time have been frustrated by the lack of linearity seen with both the time and the OD variables. Here,

$$\mathrm{PDL} = \frac{(D_0 - D)}{D_0} \times 100\,\% \,. \tag{1}$$

This difficulty can be overcome if the optical density measurement is transformed into a reflectance value, R. As the number of dots in a given area on a printed sample increases, the fraction of the media covered by these dots increases in a linear fashion until the printed dots begin to overlap, at which point the relationship becomes nonlinear. An example of this relationship is shown in Figure 3 based on 30 μm dots printed at 1200 dpi dot spacing. In this graph, the printed area of the patch increases nonlinearly with ink coverage. If the dots are assumed to be of uniform density, the reflectance value should be proportional to the fraction of the patch not covered with printed ink. This value, then, can be used to construct a model of the fading behavior of the ink-media system under consideration. This relationship is given by Equation (2), where a is related to the intensity of the ink and is analogous to the extinction coefficient and b is an offset value contributed by the media,

$$1 - R = 1 - \frac{1}{10^{\mathrm{OD}}} = a\theta_D + b. \tag{2}$$

Once this transformation is made, it becomes possible to employ a powerful technique, Langmuir-Hinshelwood-Hougen-Watson kinetic modeling typically employed in the modeling of catalytic reactions, to develop a model of the fading behavior exhibited by many ink-media systems.[21–23] The light induced fading can be modeled as a series of two steps, as depicted in Figure 4. First, an activated species is adsorbed from the atmosphere in an equilibrium process. This step is physically relevant, as numerous studies have suggested the importance of photochemically generated singlet oxygen, atmospheric ozone, or other activated species in the fading of magenta dyes.[26–32] Then, the second reaction step can be modeled as a first order reversible surface reaction that results in the formation of a colorless degradation product. It is important to note that this model surface reaction is a simplification of the multiple possible reactions that have been shown to occur.[14,25,33–35] For this analysis, however, combining these multiple reaction pathways provides an adequate approximation for modeling the fading behavior accurately.

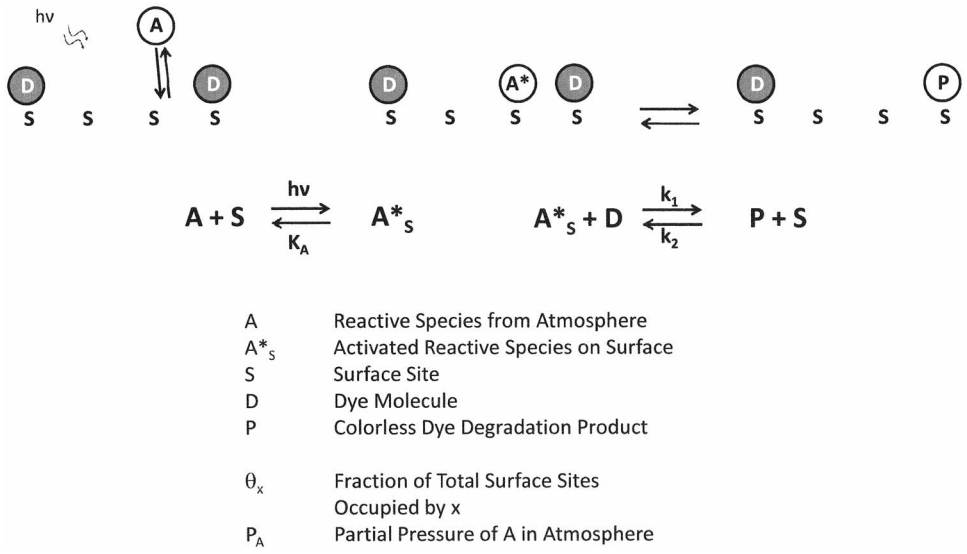

Figure 4. Schematic representation of two-step mechanism used to model light fading. First, the reactive species reversibly adsorbs to the surface from the atmosphere. Then, a dye molecule on the surface reacts reversibly with this adsorbed species to form a colorless product.

Assuming that the total number of surface sites is finite and constant, we can represent the site balance on the surface sybolically as shown in Figure 4, and obtain Equation (3),

$$\theta_A + \theta_D + \theta_P + \theta_V = 1. \tag{3}$$

The terms used here and in the following expressions are defined in Fig. 4. Using the pseudo-steady-state approximation for the concentration of the reactive species from the atmosphere (A) leads to Equation (4),

$$K_A = \frac{\theta_A}{P_A \theta_V}. \tag{4}$$

The rate equation for the reversible surface reaction is given by Equation (5),

$$\text{rate} = k_1 \theta_A \theta_D - k_2 \theta_P \theta_V. \tag{5}$$

Combining and simplifying Equations (3)–(5) we can express this rate equation in the form of Equation (6),

$$\text{rate} = -\frac{d\theta_D}{dt} = \frac{[\theta_D(k_1 K_A P_A + k_2) - k_2 \theta_{D_0}](1 - \theta_{D_0})}{1 + K_A P_A}. \tag{6}$$

Integration of Equation (6) with the appropriate initial condition ($\theta_D = \theta_{D_0}$ at time $t=0$) yields Eq. (7) which requires determination of two independent parameters α and β for complete solution:

$$\theta_D = \theta_{D_0}[\alpha + (1 - \alpha)e^{-(1-\theta_{D_0})\beta t}], \tag{7}$$

$$\alpha = \frac{k_2}{k_1 K_A P_A + k_2}, \tag{8}$$

$$\beta = \frac{k_1 K_A P_A + k_2}{1 + K_A P_A}. \tag{9}$$

Solution of Equation (9) for the 10 ink/media combinations under consideration using a least-squares analysis in MICROSOFT EXCEL® yields values for the parameters α and β. Using data with OD_0 from 0.25 to 1.7, an excellent fit is obtained for all ink/media combinations. Figure 5 shows representative data: model fits to experimental data for two ink/media combinations. While there is some deviation from the model for the very high and very low starting optical density patches, the model fits very well in the region used to determine fade end points. The resulting coefficients obtained after the completion of all fading experiments are given in Table III.

The most powerful aspect of this analysis is its robustness over time. Once an ink/medium combination is modeled, the values for α and β vary little with time. This stability allows the accurate prediction of future fading behavior, as shown in Figure 6. Values for α and β were determined after each fade measurement and used to predict

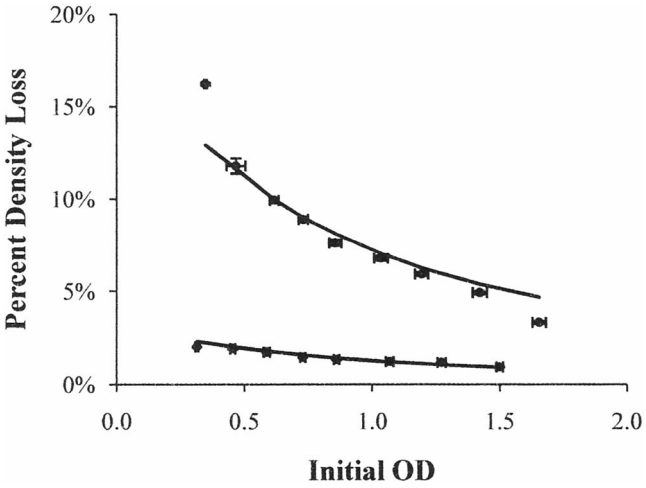

Figure 5. Comparison between two parameter model and experimental fade data for two ink/media combinations, ink D3 on media M1 after 384 h of accelerated fade (bottom) and ink D2 on Media M2 (top) after 990 h of accelerated fade. Error bars represent ±1 standard deviation.

Table III. Values of α and β for two parameter model obtained after completion of fading for all ink/media combinations.

Ink	Media	Fade duration (h)	α	β
D1	M1	552	0.66	0.015
D2	M1	990	0.42	0.0013
D3	M1	1680	0.24	0.00024
D4	M1	216	0.69	0.093
D5	M1	48	0.47	0.17
D1	M2	720	0	0.0013
D2	M2	1680	0	0.00026
D3	M2	1680	0.56	0.00024
D4	M2	552	0.63	0.015
D5	M2	216	0.48	0.027

the fade after ten weeks of accelerated fading. The data collected after 48 h of fading fails to predict the results of the accelerated fading accurately by itself. Once multiple time points have are included in the model, however, the predicted values rapidly converge. The power of this model is evident, as it accurately predicts the fade behavior well into the future. After 216 h of accelerated fading, the performance of this ink/media combination can be predicted out to 1680 h of accelerated light induced fading with an average error of less than 1.3%.

For a simpler analysis, it is possible to model the surface reaction as irreversible and reduce the kinetics to the simple one-parameter model given by Eq. (10):

$$\theta_D = \theta_{D_0} e^{-(1-\theta_{D_o})\beta t}. \tag{10}$$

Values for each parameter, based on a regression including all pertinent data prior to cessation of fading, are given in

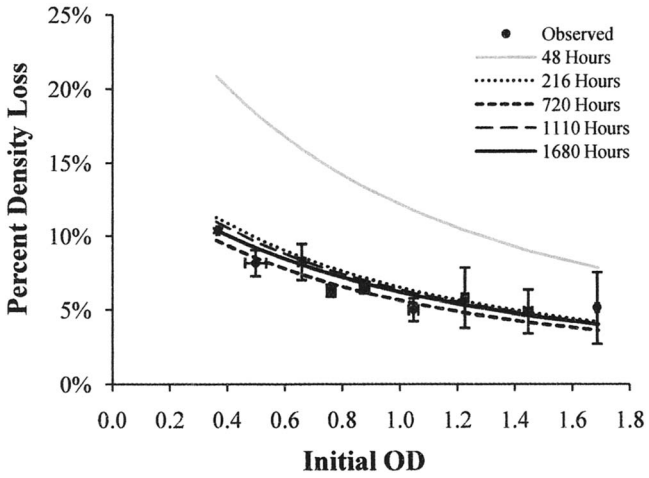

Figure 6. Observed fade data for ink D3 on media M2 after ten weeks of accelerated fade. The curves represent model predictions made at earlier time points. Error bars represent ±1 standard deviation.

Table IV. Observed values of β and Light fade factor for one parameter model obtained after completion of fading for all ink/media combinations.

Ink	Media	Fade duration (h)	β	Light fade factor
D1	M1	552	0.0029	5.83
D2	M1	990	0.00085	7.07
D3	M1	1680	0.00018	8.61
D4	M1	216	0.0097	4.64
D5	M1	48	0.055	2.90
D1	M2	720	0.0013	6.65
D2	M2	1680	0.00026	8.27
D3	M2	1680	0.00010	9.20
D4	M2	552	0.0036	5.62
D5	M2	216	0.0097	4.63

Table IV. These values vary over 3 orders of magnitude and present the opportunity to describe a "light fade factor," defined as $-\ln(\beta)$ that describes fading of an ink/medium combination. In all cases where the fading proceeded for greater than four weeks, the values for this light fade factor exhibited remarkable stability (RSD $\leq$5.3%). This time independence suggests that, using this light fade factor, it is possible to make quantitative comparisons between ink/media systems based on short-term fading data. While the predictive power of this model is less robust than the two parameter model, it may serve as an easily communicated method to describe the system. Such a figure of merit can be used to make meaningful comparisons that describe the relative lightfastness of ink/media systems based on a data collected at various time points from various test facilities.

Using a simple linear regression, where the light fade factor of the system is simply the sum of the factors for the ink and media, the contributions of the ink and the contribution of the media can be separated and a light fade factor assigned to each component. As shown in Eq. (11) this analysis allows for the determination of the individual contributions to the light fade resistance for the ink and the media:

$$-\ln(\beta)_{\text{system}} = -\ln(\beta)_{\text{ink}} - \ln(\beta)_{\text{media}}. \quad (11)$$

The results of this analysis, included in Tables I and II, allow for quantitative values to be assigned rather than relying on qualitative description to describe an ink or dye. It may be beneficial to include a third term to address the impact of specific ink/media interactions; the experimental design employed in these experiments does not allow a thorough investigation of this correlation, however, because of the relatively small sample size. The general agreement between the predicted and observed values, however, suggests the utility of such a comparison.

CONCLUSION

Current methods to predict long-term light stability of images printed using ink jet technology rely on long-term fade testing using accelerated fade methods. Even in these highly accelerated tests, it can take several weeks to obtain meaningful results for particular ink/media systems. By employing a simple kinetic model of light fading, it is possible to predict the results of long-term accelerated light fade testing in a much shorter period of time. It is also possible, using a simplified model, to compare inks and media independently to assess their permanence properties. These methods allow the rapid comparison of ink/media combinations and represent the opportunity to optimize formulations in a much more rapid and efficient manner than is currently employed. These methods have been applied to select magenta ink formulations on two representative media.

A more thorough understanding of this model can best be obtained by extending its application to cyan and yellow inks and then investigating its application to secondary and tertiary colors printed on various media. Extending the application to alternate media types (especially porous media) alternate colorants (including dye mixtures and pigments) and to different permanence tests (ozone-fastness, humidity-fastness, catalytic fade, etc.) will also be instructive.

ACKNOWLEDGMENTS

The author would like to thank Lexmark International for supporting this work. In addition, much appreciation is extended to Tom Dziubla in the University of Kentucky Department of Chemical and Materials Engineering for his assistance and advice.

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