Further Investigations into Accelerated Light Fade Reciprocity of Inkjet Photographic Prints

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Abstract

The use of high-intensity illumination to accelerate the fade of photographic prints in order to predict long-term performance under ambient illumination rests on the assumption that the Reciprocity Law is valid over the range of illumination intensities between the accelerated and ambient conditions. Simply stated, the Reciprocity Law predicts that the extent of a light-induced chemical reaction, e.g., fade of an inkjet colorant, is directly proportional to the cumulative exposure (intensity x time) independent of the illumination intensity. Reciprocity failure is said to occur when equivalent cumulative exposures at different intensities result in differing amounts of fade. In this study we investigated the reciprocity behavior of a variety of ink-media combinations in response to high- (80 klux) and low- (5.4 klux) intensity polycarbonate-filtered fluorescent illumination. We will also briefly review recent results for high- (50 klux) and low- (5.4 klux) intensity glass-filtered xenon illumination.

Introduction

The long-term stability of photographic images has long been of interest in the field of imaging and photography. There are four main environmental variables known to impact image stability: light, heat, humidity, and air pollutants, such as ozone [1,2]. Although the only error-proof method for testing image permanence is natural aging under "real-world" levels of these variables, the high stability of modern photographic products makes testing under ambient conditions too lengthy to be practical. Thus, a widely used alternative to natural aging is accelerated aging, in which the environmental factors are held at levels considerably greater than ambient, forcing the test sample to a failure point in a much shorter period of time. In the case of accelerated light fade testing, this approach relies heavily on the assumption that image degradation for samples exposed to very high-intensity illumination for relatively short time intervals can be directly related to product behavior when exposed to an ambient light level for longer times. This relationship is known as the Reciprocity Law.

The Reciprocity Law, originally proposed by Bunsen and Roscoe in 1862 to describe light-induced chemical reactions, states that the product of a photochemical reaction is determined simply by the total exposure, that is, by the product of irradiance and time, and is independent of the two factors separately [3]. In the context of light-induced fade of photographs, the Reciprocity Law can be described such that the change in density (ΔD) resulting from high-intensity illumination (HI) for a short period of time is equal to the change in density that results from low-intensity illumination (LI) for a long period of time, given that the two conditions yield an equal amount of cumulative exposure, as defined by the product of intensity and time. This relationship can be expressed mathematically as:

$$\Delta D_{LI} = \Delta D_{HI} \quad \text{(at equivalent cumulative exposures)} \qquad (1)$$

Unfortunately, this law can fail as the difference between HI and LI becomes increasingly large. This is known as *reciprocity failure*. Because image degradation resulting from treatment under LI test conditions is considered more representative of change occurring under ambient conditions (less acceleration), reciprocity failure is attributed to the HI condition, and can be expressed as follows:

$$\Delta D_{LI} = R_f(\Delta D_{HI}) \qquad (2)$$

Here, R_f represents a constant or "reciprocity" factor, by which the ΔD_{LI} and the ΔD_{HI} data are related. Rearranging this equation to solve for R_f, we get:

$$R_f = \frac{\Delta D_{LI}}{\Delta D_{HI}} \qquad (3)$$

Note that R_f will assume a value of 1.0 if the Reciprocity Law holds, and the LI and HI test conditions yield an equal change in density at equivalent cumulative exposures. Alternatively, R_f will assume a value greater than 1.0 if the LI condition yields more density change than the HI condition. Finally, R_f will assume a value less than 1.0, if the HI condition yields more density change than the LI condition.

It is critical that any test of reciprocity failure must ensure that the effect of light be isolated from all other known environmental factors. For example, previous reports of gross reciprocity failure for inkjet prints [4,5] were found to be largely ascribable to low and/or variable levels of ambient pollutants, such as ozone, present in the test chambers [6], which, over the much longer duration low-intensity light fade tests, can contribute significantly to the overall observed fade. On the other hand, the long-term effects of ambient humidities higher than about 60% RH are known to result in measurable *increases* in color density, which in turn could be manifested as less change in density under the longer duration low-intensity tests [7–9]. Situations such as these, where factors other than light itself are contributing to the observed lack of reciprocity between high- and low-intensity exposures, have been termed *apparent* reciprocity failure [6].

We have recently undertaken a study of light fade reciprocity for a wide variety of inkjet materials using both fluorescent (5.4 vs

80 klux) and xenon illumination (5.4 vs 50 klux) under conditions designed to isolate the effect of light on the test samples from the other known environmental factors. In this report we summarize the calculated reciprocity factors and discuss the significance of reciprocity failure on the prediction of long-term light fade behavior under ambient illumination conditions. In a separate report, we have proposed a method for conducting relatively abbreviated low-intensity light fade tests to accurately estimate R_f, which can then be used to "correct" the high-intensity data [10]. The concept of reciprocity factors has also been demonstrated for accelerated ozone-fade testing [11].

Materials and Methods

In the first phase of this study, carried out in 2003–2004, the inkjet photo papers listed in Table 1 were printed using the printers and inks listed in Table 2. In the second phase of this study, carried out in 2005–2006, the inkjet photo papers listed in Table 3 were printed using the printers and inks listed in Table 4. Papers and inks were freshly obtained and are representative of products that were available in retail channels at the time of each phase of the study. Not all possible combinations of media and ink were printed.

The test targets and methods have been described previously [4,12–14]. In the first phase, identical samples were treated in both 5.4- and 80-klux polycarbonate-filtered fluorescent chambers maintained at 23 ± 2°C, 50 ± 3% RH, and <2 ppb ozone. In the second phase, identical samples were treated in duplicate in both 5.4- and 50-klux glass-filtered xenon chambers maintained at 23 ± 2°C, 50 ± 3% RH, and <2 ppb ozone. All samples were separately evaluated for ozone, humidity, and thermal stability.

Table 1: Glossy inkjet media used in the first phase of this study

Brand	Description	Type*
HP	Premium Plus Glossy	S
Epson	Premium Glossy	P
Epson	ColorLife	S
Canon	Photo Paper Pro	P
JetPrint	Photo Pro	P
Ilford	Printasia	P
Kodak	KODAK Premium Picture Paper	S
Kodak	KODAK Ultima Picture Paper (Satin)	S
Kodak	KODAK Ultima Picture Paper (Glossy)	S

**S = swellable; P = porous*

Table 2: Printers and inks used in the first phase of this study

Model	Ink Cartridges	Type*
HP 3820	HP78	D
HP 5550	HP56/HP58	D
Epson 825	T007/T008	D
Epson 960	T033X20	D
Lexmark Z65	Lexmark 83	D
Canon i550	BCI-3X	D
Canon i950	BCI-6X	D

**D = dye*

Table 3: Glossy inkjet media used in the second phase of this study

Brand	Description	Type*
HP	Premium Plus Glossy	S
Epson	Premium Glossy	P
Lexmark	Premium Photo Paper	S
Canon	Photo Paper Pro	P
Kodak	KODAK Professional Inkjet Paper	P
Kodak	KODAK Ultima Picture Paper (Glossy)	S

**S = swellable; P = porous*

Table 4: Printers and inks used in the second phase of this study

Model	Ink Cartridges	Type*
HP 5740	HP97	D
HP 8450	HP97/HP99	D
Epson R300	T0048X20	D
Epson R800	T0054X20	P
Canon i950	BCI-6X	D
Lexmark Z816	Lexmark 33/Lexmark 31	D/P

**D = dye; P = pigment*

For the reciprocity calculations, we limited our analysis to the fade of pure primary colors. Reciprocity factors, R_f, were calculated according to Equation 3. To be included in the statistical analysis, the following criteria had to be met:

- At least 15% density loss from a 1.0 initial density must be observed under both high- and low-intensity conditions.
- The kinetics, e.g., linear or logarithmic, must be common under both conditions with $R^2 \geq 0.95$.
- The observed density changes must not be confounded by measurable sensitivity to ozone, humidity, or thermal treatment over the duration of the light fade treatments.

Results and Discussion

Polycarbonate-Filtered Fluorescent Conditions

It has been standard practice at Eastman Kodak Company to conduct accelerated light fade testing under at least two intensities in order to ascertain whether reciprocity concerns exist [4,13]. During early studies of the light fade of inkjet photographic prints significant deviations from reciprocity have been reported [4,5], which, upon further evaluation, were found to be largely due to the presence of "dark fade" processes [6]. Recently, it has been proposed "that a 'generic' reciprocity failure correction of perhaps a factor of 3 be considered" [15].

In light of this suggestion, we undertook a critical evaluation of our extensive polycarbonate-filtered fluorescent database on inkjet photographic prints to see if such a large correction factor is warranted. As noted above, it is important that all other potential sources of *apparent* reciprocity be controlled and eliminated from such an evaluation. For this phase of the study, we limited our evaluation to over 100 unique dye-media combinations that were printed and dried under the same conditions using the same lots of ink and media, and which were submitted for both high- (80 klux) and low- (5.4 klux) intensity testing at about the same time. After applying the criteria listed above, we were left with 64 unique ink-media combinations for which true reciprocity factors could be calculated. Of these 64 combinations, 24 were found to fade by apparent 0^{th} order (linear) kinetics, and 40 exhibited apparent 1^{st} order (logarithmic) kinetics.

Figure 1 shows an example of an ink-media combination that illustrates one of the higher levels of reciprocity failure with a logarithmic decay. Also shown in Figure 1 is one of the tests for true reciprocity based on Equation 3: R_f should be a constant as a function of cumulative exposure [10]. In this example, R_f was found to be 1.2 when calculated at either 25.0 or 29.0 mlux-hr of cumulative exposure.

Figures 2 and 3 summarize the distributions of calculated reciprocity factors for ink-media combinations that exhibit linear and logarithmic decay, respectively. A couple of interesting observations can be made based on the data shown in Figures 2 and 3. First, and perhaps most surprising, is that there is a fairly normal distribution of R_f with a mean and median both close to 1.0 for both linear and logarithmic systems. This means that there are nearly as many examples of ink-media combinations that fade slower under lower intensity illumination ($R_f < 1$) as there are that fade faster ($R_f > 1$). Second, the magnitude of reciprocity failure ranges from 0.8–1.8 for linear systems and from 0.7–1.3 for logarithmic systems, which is far less than the generic factor of 3 that has been proposed.

It is important to understand the implication of reciprocity failures on print-life estimates for linear vs logarithmic systems. Typically, print-life estimates are made by running the light fade test until a specified amount of density change occurs, which is commonly in the 20–40% range of the starting density, i.e., 0.2–0.4 density loss from a 1.0 initial density. This is often referred to as an "end-point" criterion. For linear fading systems, the effect of reciprocity failure, as measured by R_f, is, by definition, equivalent whether the test is run to a constant cumulative exposure (x-axis) or to a constant density change (y-axis). In other words, an R_f of 1.3 would correspond to a 1.3X greater density change under low-intensity conditions at a given cumulative exposure. Conversely, the sample would reach a given density change at 1.3X greater cumulative exposure for the high-intensity condition.

However, for logarithmic fading systems, although R_f is constant independent of cumulative exposure [10], the impact of reciprocity failure on the cumulative exposure necessary to reach a given density change is variable. For greater density changes, the ratio of cumulative exposures between high and low light intensities gets progressively larger. For example, for the logarithmic fading system illustrated in Figure 1 ($R_f = 1.2$), if we look at a density change criterion of 20%, the cumulative exposure ratio is found to be about 1.8, i.e., it takes a 1.8X greater cumulative exposure to reach a 20% density change at the high-intensity condition compared to the low-intensity condition. On the other hand, if we look at a density change of 40%, the cumulative exposure ratio increases to 2.2. In either case, this is still much less than the generic 3X correction factor that has been proposed, especially considering that this was one of the worst-case logarithmic reciprocity failures that were observed. This also illustrates the danger of calculating a "correction factor" based on the ratio of cumulative exposures at high and low intensities required to produce a given density change.

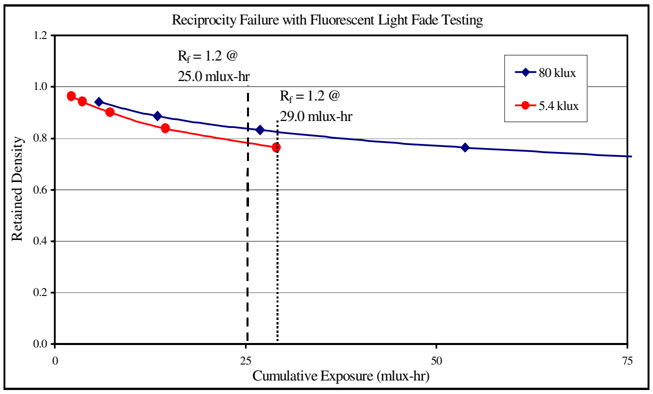
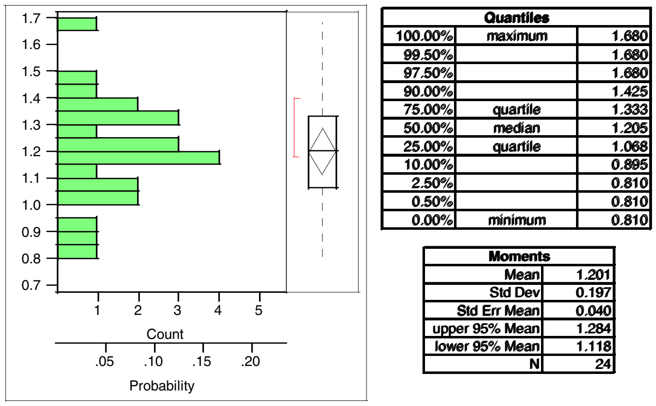


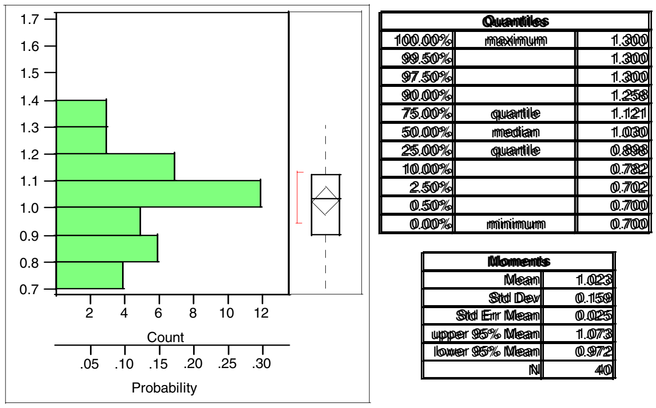
***Figure 1**. Example of reciprocity failure for an ink-media combination under polycarbonate-filtered fluorescent conditions (Phase 1) illustrating logarithmic decay and constant R_f.*



Quantiles		
100.00%	maximum	1.680
99.50%		1.680
97.50%		1.680
90.00%		1.425
75.00%	quartile	1.333
50.00%	median	1.205
25.00%	quartile	1.068
10.00%		0.895
2.50%		0.810
0.50%		0.810
0.00%	minimum	0.810

Moments	
Mean	1.201
Std Dev	0.197
Std Err Mean	0.040
upper 95% Mean	1.284
lower 95% Mean	1.118
N	24

***Figure 2.** Statistical summary of R_f for linear fading ink-media combinations under polycarbonate-filtered fluorescent conditions.*



Quantiles		
100.00%	maximum	1.300
99.50%		1.300
97.50%		1.300
90.00%		1.258
75.00%	quartile	1.121
50.00%	median	1.030
25.00%	quartile	0.898
10.00%		0.782
2.50%		0.702
0.50%		0.700
0.00%	minimum	0.700

Moments	
Mean	1.023
Std Dev	0.159
Std Err Mean	0.025
upper 95% Mean	1.073
lower 95% Mean	0.972
N	40

***Figure 3**. Statistical summary of R_f for logarithmic fading ink-media combinations under polycarbonate-filtered fluorescent conditions.*

Glass-Filtered Xenon Conditions

Recent studies have concluded that the average illumination in the display environment of the typical home is more closely approximated by filtered xenon than by fluorescent lighting [16,17]. The spectral energy distribution of a glass-filtered xenon lamp comprises significantly more energy in the blue and near-UV regions (300–500 nm) than either filtered or unfiltered fluorescent illumination [17]. Therefore, it was of interest to further investigate the reciprocity behavior under low- and high-intensity glass-filtered xenon light fade conditions to see if the same trends were observed.

Figure 4 shows an example of an ink-media combination with logarithmic behavior for which R_f <1. Again, R_f is essentially constant over the range of interest. Out of 54 possible primary colorant-media combinations included in the second phase, 32 met the criteria listed above for inclusion in the statistical analysis, and 29 out of those 32 were found to exhibit linear kinetics. Figure 5 summarizes the statistics for the 29 linear fading systems.

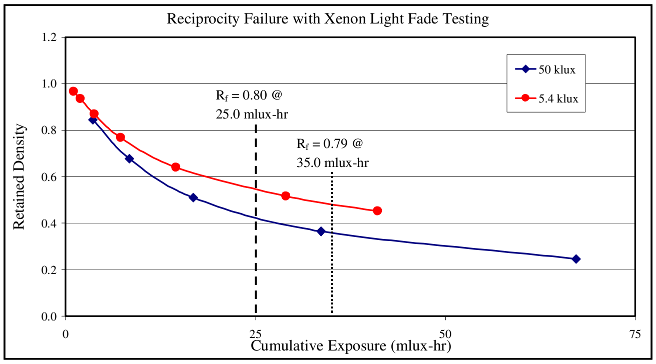
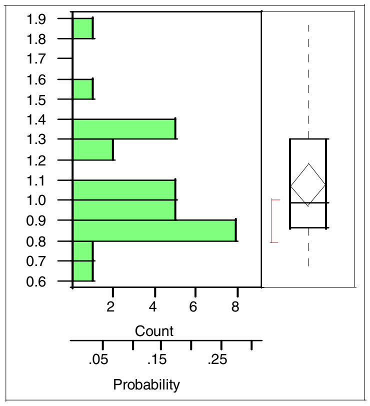


***Figure 4**. Example of reciprocity failure for an ink-media combination under glass-filtered xenon conditions (Phase 2) for which R_f is less than 1.*



Quantiles		
100.00%	maximum	1.860
99.50%		1.860
97.50%		1.860
90.00%		1.390
75.00%	quartile	1.300
50.00%	median	0.990
25.00%	quartile	0.865
10.00%		0.830
2.50%		0.650
0.50%		0.650
0.00%	minimum	0.650

Moments	
Mean	1.075
Std Dev	0.273
Std Err Mean	0.051
upper 95% Mean	1.179
lower 95% Mean	0.971
N	29

***Figure 5**. Statistical summary of R_f for linear fading ink-media combinations under glass-filtered xenon conditions.*

The results shown in Figure 5 reveal a slightly less normal distribution compared to the linear fading systems observed for the first phase, with a mean of 1.075 and a median of 0.990. However, the general conclusions are similar: there are a significant number of ink-media combinations with R_f <1, and there are no examples of R_f >2. For the three logarithmic fading systems the R_f values were 0.79, 0.87, and 1.23. These results are also consistent with the results for the first phase. At this time it is unclear why the glass-filtered xenon conditions result in such a higher relative proportion of linear kinetics compared to the first phase results.

Conclusions

This study of reciprocity behavior for accelerated light fading indicates that widespread reciprocity failure is not evident under the range of illumination conditions used for this study. In fact, for the nearly 100 unique colorant-media combinations for which true R_f values were calculated, the overall mean and median values of R_f were found to be very close to 1.0. However, for product performance claims of light-fade resistance based on a single high-intensity exposure condition, it may be prudent to assume some level of reciprocity failure. At the 90th percentile, an estimate of R_f in the range of 1.3–1.4 appears to be reasonably conservative. A recommended alternative is to run a relatively brief low-intensity light fade test in combination with a highly accelerated test condition, with sufficient replication and measurement frequencies, to quickly and accurately calculate R_f for a given ink-media combination, and then to apply this factor to “correct” the high-intensity fade results [10]. Clearly, a generic 3X correction factor is not warranted based on the results of this study.

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Biography

Douglas Bugner received a Ph.D. in Organic Chemistry from UCLA in 1982. He is currently Senior Laboratory Head, Ink and Media Lab, Graphics Inkjet Platform Center, Eastman Kodak Company. He holds 58 U.S. Patents, and has authored over 40 scientific publications.