Sensitivities of Kodak's Thermal Dye Transfer Prints to Environmental Factors

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Abstract

Increasingly, digital photographers employ the thermal dye transfer system to produce their color hard copy prints. The Kodak Professional Ektatherm Xtralife™ three-color ribbon (donor) and receiver in Kodak's kiosk picture making system offers a convenient method for producing durable, long-lasting high-quality prints from digital files. This paper will discuss the sensitivities of the Kodak Xtralife system to key environmental factors—light, temperature, relative humidity, and gaseous pollutants. Gathering data to characterize print sensitivity to temperature has proven to be a long process because of the incompatibility of the thermal dye transfer print's physical characteristics with the high end of the temperature range used in accelerated Arrhenius testing. However, reasonable data can be generated if the prints are tested at temperatures near or below the glass transition temperature of the receiver matrix.

Introduction

Thermal dye transfer systems create color prints by using heat to sequentially transfer yellow, magenta, and cyan dyes from a donor ribbon to a resin-coated paper receiver. In the final step, a laminate overcoat layer is transferred to the receiver to act as a protective overcoat for the final print.

Under typical storage conditions, Kodak's thermal dye transfer prints exhibit very slow rates of density loss that are, practically, immeasurable, requiring accelerated conditions to produce estimates of density loss that can be extrapolated to typical home storage conditions. Similar to the colorants in many color hard-copy printmaking systems, the Kodak dyes exhibit density loss when the print is exposed to such environmental factors as temperature, light, or gaseous environmental pollutants such as ozone. However, these prints exhibit little or no sensitivity to relative humidity (RH) because of the protective overcoat.

Determination of the sensitivity of Kodak's thermal dye transfer prints to light, relative humidity, and gaseous environmental pollutants is straightforward, requiring that a sample print receive exposure to high levels (vs. typical home display conditions) of the specific factor. High levels typically are chosen to reduce the amount of time needed for the sample print to exhibit significant amounts of density loss - 30% or more. However, testing at high temperature, high light intensity, or high concentrations of gaseous pollutants might lead to estimates of the rate of density loss that do not correlate well to results obtained from lower factor levels, which are closer to typical home display conditions, and this calls into question the ability to extrapolate accelerated testing to typical home display conditions, which can be orders of magnitude lower than the levels employed in the accelerated testing. One way to assess the potential of an accelerated test to yield poor extrapolative power involves running the test at several levels of the specific factor and comparing the predicted density-loss endpoint for each level at equivalent "intensity X time." For example, a light-fading test performed at 100,000 lux for 20 days will produce the same cumulative exposure as a light-fading test performed at 10,000 lux for 200 days under the same illuminant. If the actual (or predicted) density losses from these two factor levels do not agree closely, the confidence around the ability to extrapolate the accelerated test data to typical home display conditions would be compromised. Such lack of agreement between tests conducted at different intensities and times but yielding the same overall cumulative exposure is called "reciprocity failure."

Measuring temperature sensitivity of the thermal dye transfer print presents a unique challenge. Historically, we have used the Arrhenius equation[1,2] to estimate the amount of time a photograph needs to remain at a certain temperature for it to exhibit a certain amount of density loss. This methodology rests on three fundamental assumptions:

1. The mechanism of density loss does not change over the range of elevated temperature conditions used to generate the fading rate estimates.
2. The system does not undergo a phase change over the temperature range of interest.
3. Not more than one competing reaction exists.

We have determined from our high-temperature print-fading tests that the thermal dye transfer print probably conforms to these assumptions over a range of relatively low elevated temperatures, effectively extending the duration of testing to a rather long time.

Temperature Sensitivity

We tested Kodak's thermal dye transfer prints at a variety of elevated temperatures in humidity-controlled dark ovens. Yellow density loss vs. time for six temperatures is shown in Figures 2 and 3. The data come from two different testing events, each comprising three different temperatures. The first event gathered densityloss data at 80°C, 70°C, and 60°C, all at 50% relative humidity (RH) (Figure 1). The second event gathered densityloss data from three lower temperatures—50°C, 45°C, and 40°C, again all at 50% RH (Figure 2).

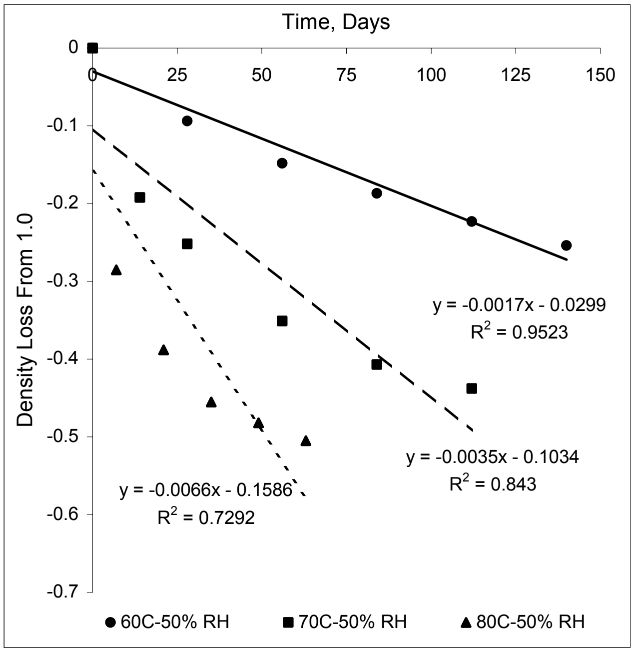

Figure 1. Yellow density loss vs. time at 80, 70, and 60°C, all at 50% RH

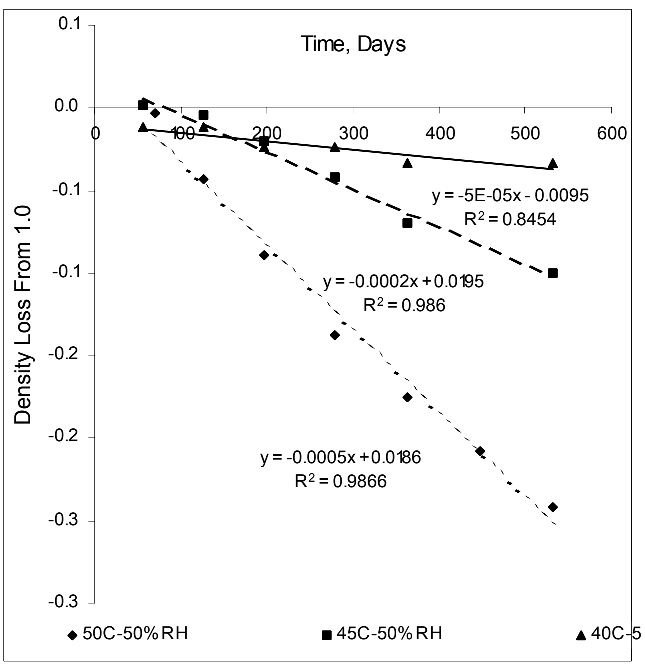

Figure 2. Yellow density loss vs. time at 50, 45, and 40°C, all at 50% RH

In the higher temperature regime, nonlinear density loss is observed, although the density loss curve at 60°C can be reasonably modeled with a simple linear function. In the lower temperature regime the lowest temperature, 40°C, does not model well with a linear function, although this probably results from the small amount of density loss observed at this temperature after 532 days. Examination of the oven-treated samples shows significant amounts of dye migration in the high temperature samples throughout the receiver structure, including the backside resin layer. This is a strong indication that the thermal dye transfer system does not conform to the basic assumptions enabling analysis of the rate data with the Arrhenius equation over the high temperature range because the receiver matrix undergoes its glass transition at a temperature above 50°C. Consequently at high oven temperatures, falsely high rates of density loss will be observed. While this causes problems in using accelerated testing to make stability predictions, the glass transition is still well above conditions normally encountered by the typical consumer.

The slope of each density loss curve, multiplied by 365 to yield a yearly rate of density loss at each temperature, was converted to its logarithm and plotted against 1/T (K). These two Arrhenius plots (Figure 3) show significant differences in their slopes, and the high-temperature linear regression does not predict the fading rate at 50°C or lower temperatures.

Given the discontinuity between high- and low-temperature dark-oven testing, determining the temperature sensitivity of the thermal dye transfer print will require two to six years of testing at temperatures below 50°C to achieve results that have reasonable predictive power for "historical" density-loss endpoints of 30% from a 1.0 color or neutral patch at "room temperature," – 24°C.

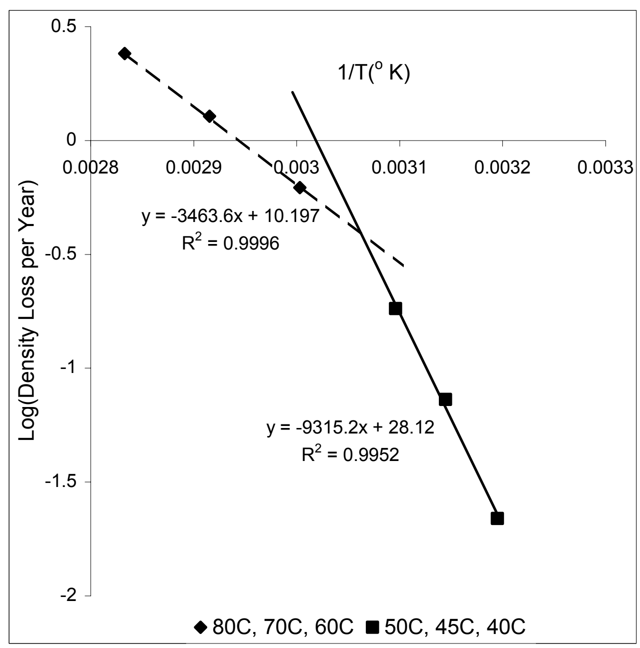

Figure 3. Arrhenius plots for the two temperature regimes—60 to 80°C and 40 to 50°C, all at 50% RH

Not wanting to wait the two to six years to begin the analysis of the lower temperature accelerated data, the current limited data may be used to estimate lower percentage losses at 24°C, using a density-loss endpoint of less than 30%. Because the dyes are so stable in this accelerated temperature test regime (40, 45, and 50°C), a density-loss endpoint of no more than 5% must be used. Applying the low temperature regression equation from Figure 3 yields the following time estimates for 5% density loss from a 1.0 color patch at 24°C; obviously, times to 30% density loss would far exceed these estimates:

Cyan	> 80 years
Magenta	> 100 years
Yellow	> 80 years

The 5% density-loss endpoint, as compared to the 30% endpoint, is a very small amount of density change and, in most cases, would be unnoticeable.

Humidity Sensitivity

We have tested thermal dye transfer prints under several relative humidity conditions—30, 50, and 70% RH at a constant temperature of 40°C. These conditions are similar to those used to assess the humidity sensitivity of Kodak Ultima picture paper.[3] C, M, and Y density changes at each RH condition were measured for 24 weeks.

The plot of cyan density loss vs. time is shown in Figure 4. Magenta and yellow density vs. time plots exhibited very similar behavior. Clearly, these prints exhibit little or no sensitivity to relative humidity.

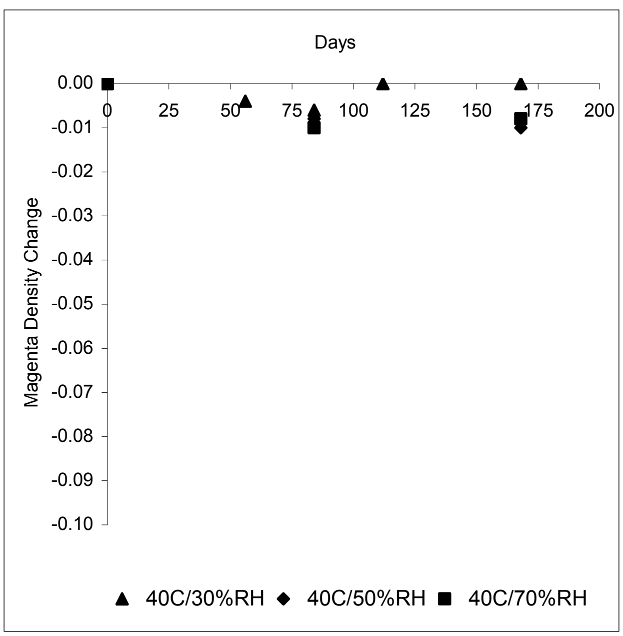

Figure 4. Cyan density loss vs. time at 30, 50, and 70% RH, all at 40°C

Light Sensitivity

We exposed the thermal dye transfer prints to fluorescent light (filtered through polycarbonate) at two intensity levels: 5.4 and 80 Klux. Achieving the same cumulative exposure at 80 Klux requires a little less than 7% of the time at 5.4 Klux. In other words, four weeks at 80 Klux yields almost the same number of megalux-hr of exposure (53.8) as 60 weeks at 5.4 Klux (54.4). Moving to still lower illuminant intensities extends the time even further. Using a 1.0 Klux UV-filtered fluorescent illuminant would require six years to reach 54 megalux-hr of cumulative exposure! The density loss curves for cyan, magenta, and yellow 1.0 color patches, and the 1.0 neutral, are shown in Figures 5 and 6, respectively. All of the density loss vs. time plots can be modeled with simple linear regressions yielding r^2 values of 0.97 or greater. Density losses from neutrals and additive primary colors (red, green, or blue) also show similar linear behavior with r^2 values of 0.95 or greater. Using the linear regression functions, we estimated the megalux-hr of exposure to reach 30% density loss for cyan, magenta, or yellow density loss from a palette of color patches that included subtractive primary colors, additive primary colors, and neutral, based on the 5.4 Klux and the 80 Klux test data. These are shown in Table 1. For each color patch, we compared the cumulative exposure estimates determined from the high- and low-intensity tests by subtracting the 5.4 Klux result from the 80 Klux result and calculating the difference as a percentage of the 5.4 Klux estimate—"Delta (%)."

Two interactions can be seen:

1. The presence of cyan dye seems to decrease the rate of either magenta or yellow density loss from neutral, green, or blue.
2. The presence of magenta dye seems to increase the rate of yellow density loss in red, but not neutral, when the cyan dye is also present.

While differences in the estimates exist between the two intensities, testing at either intensity identified yellow density loss from red, and magenta density loss from magenta or red as exhibiting the highest sensitivity to light.

The agreement between the estimates for the limiting density loss suggests that these estimates could be reasonably applied to lower intensity conditions. Home environments have been measured at less than, or equal to, 137 lux during the daytime cycle at the 90th percentile of the distribution.[4] Using the 24 hr intensity estimate of 64.8 lux (12 hr per day at 137 lux) and the 5.4 Klux test results, it would take 97 years to reach 30% density loss for the limiting color—yellow density loss from red—under a similar illuminant.

Table 1: MegaLux-hr Estimates to 30% Loss

Density	Patch ID	5.4 Klux	80 Klux	Delta(%)
Cyan	1.0 Cyan	231	270	17
Cyan	1.0 Neutral	167	250	49
Cyan	1.0 Green	229	300	31
Cyan	1.0 Blue	177	231	31
Magenta	1.0 Magenta	88	72	–17
Magenta	1.0 Neutral	371	330	–11
Magenta	1.0 Red	87	80	–8
Magenta	1.0 Blue	332	297	–10
Yellow	1.0 Yellow	156	183	17
Yellow	1.0 Neutral	303	332	9
Yellow	1.0 Red	55	50	–9
Yellow	1.0 Green	504	496	–2

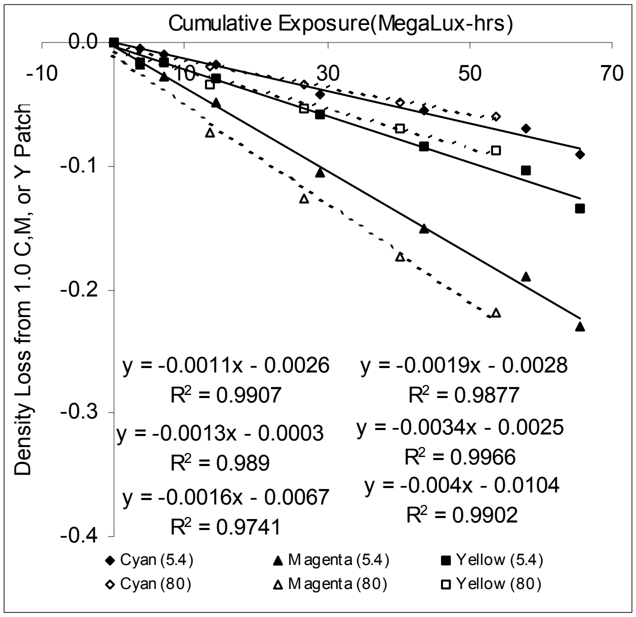

Figure 5. Density loss from C, M, or Y patches of 1.0 initial density vs. cumulative megalux-hr at two intensities—5400 and 80,000 lux.

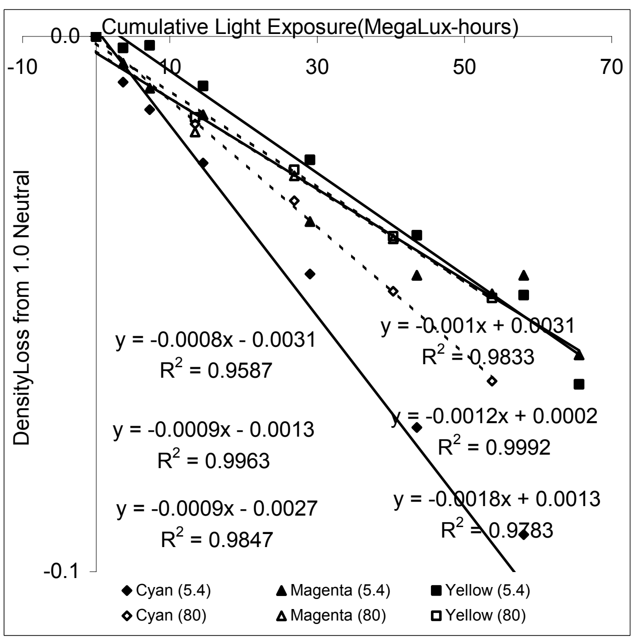

Figure 6. Density loss from neutral patch of 1.0 initial density vs. cumulative megalux-hr at two intensities—5400 and 80,000 lux

Reciprocity and Apparent Reciprocity

Looking at the subtractive primaries in Table 1 and comparing the 80 Klux to the 5.4 Klux results, one sees generally good reciprocity law behavior with only small reciprocity law deviations between the higher and lower intensity conditions. Interestingly, one also sees small deviations in both directions, where, for example, the higher intensity slightly over predicts time to the endpoint for the cyan and yellow, but slightly under predicts time to the endpoint for the magenta. Moving from the subtractive primaries to either the neutral or additive primaries, an interactive variable has been added (mixing of the colorants) that potentially changes the relationship between the high- and low-intensity test. To ensure that this is unique to the light-fastness testing, evaluation of the density loss from neutrals, and subtractive and additive primary colors must be done in dark-oven testing. For our thermal dye transfer system, dark-oven testing shows no differences in fading rate as a function of color. However, without such confirming dark-oven data the differences between high- and low-intensity light-fading tests cannot necessarily be attributed only to reciprocity law failure. Unlike many digital output media, this was not a concern for traditional silver halide materials because the colorants remained in separate layers and could not interact. The term “apparent reciprocity failure” could reasonably be applied, indicating that other non-light reactions might be taking place.

Regardless, two important conclusions emerge:

1. Testing at both higher and lower light intensities is critical, and extrapolations should be based on the condition that most closely simulates the normal usage environment.
2. Given the range of deviation from the reciprocity law demonstrated within the Kodak Xtralife system, more than one reciprocity factor would need to be calculated for this system, if one were to try to account for this phenomenon in the extrapolation to typical home display conditions, and this could well be true for other systems.

Ozone Sensitivity

We have examined the sensitivity of Kodak’s thermal dye transfer prints to ozone at three different “accelerated” ozone concentrations, 5, 1, and 0.1 ppm. The cyan dye seems to exhibit the greatest sensitivity to ozone (Figure 7). Here, cyan density loss is plotted against cumulative ozone ppm-hr of exposure as a way of normalizing the concentration differences. At 5 and 1 ppm, cyan density loss is modeled reasonably well by a simple linear function of cumulative ozone ppm-hr, although at 0.1 ppm, too little density loss has occurred (Figure 8). Both of the higher ozone concentration conditions yield similar slopes for density loss. Using the slopes from a 5 ppm exposure, we can estimate the density loss for each of the three density channels after 100 years at a “typical home display condition” of 10 ppb exposure[5] to ozone:

Cyan	=	0.09
Magenta	=	0.02
Yellow	=	0.04

At less than a hundredth of a density unit loss per decade, the excellent resistance to ozone exhibited by Kodak’s thermal dye transfer prints is also derived from the presence of the protective laminate, which limits contact of gaseous pollutants with imaging dyes. As with humidity, the presence of the protective laminate allows the thermal dye transfer media to provide a high level of durability toward these environmental factors. This is much higher than that found in many other non-traditional digital media, providing a significant stability and durability benefit to the user.

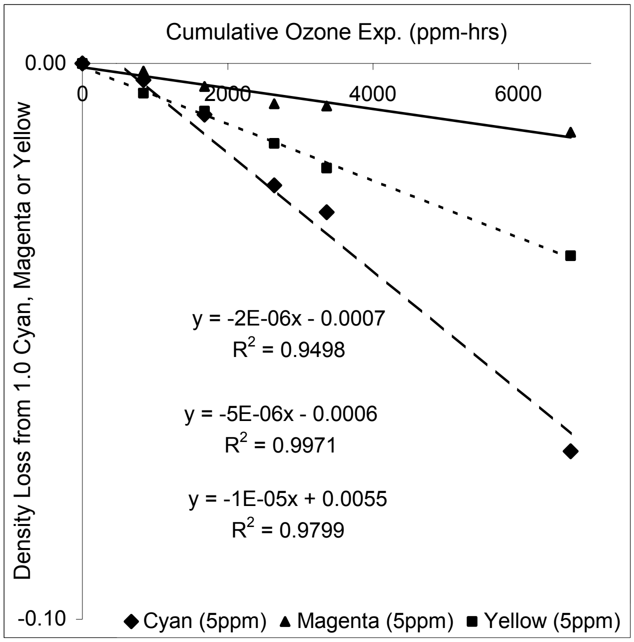

Figure 7. C, M, and Y density losses from subtractive primary color patches of initial starting density of 1.0 vs. cumulative ozone ppm-hr at 5 ppm ozone concentration

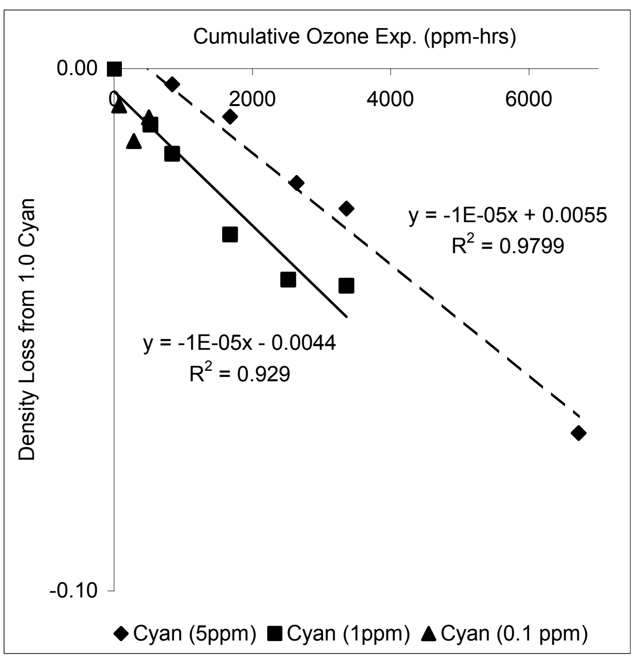

Figure 8. Cyan density loss from 1.0 cyan patch vs. cumulative ozone ppm-hr at 5 and 1 ppm of ozone *Note: Insufficient density loss at 0.1 ppm to perform linear regression*

Summary

Similar to all types of color prints, Kodak's thermal dye transfer prints exhibit sensitivity to the ubiquitous environmental factors of temperature, light, and ozone, but they exhibit virtually no sensitivity to humidity. Careful consideration must be given to the physical properties of the print media in order to derive meaningful results from accelerated test conditions. For thermal dye transfer prints, this means that temperature sensitivity testing must be done at temperatures near or below the glass transition temperature (T_g) of the receiver matrix, substantially increasing the duration of the tests. Because of the relative lack of temperature sensitivity data, we have elected to not report numerical image permanence estimates to reach a specific set of endpoint criteria for Kodak's thermal dye transfer prints. The available data on all four environmental factors, however, provide high confidence that these prints will last a lifetime in typical home display and storage conditions. Kodak's thermal dye transfer prints exhibit different rates of magenta and yellow density loss in light-fastness testing, depending on the presence or absence of cyan dye with saturated reds representing the most extreme environment for magenta or yellow density loss. This reinforces the need to test more than neutrals and subtractive primary colors for light sensitivity.

References

1. C. C. Bard, G. W. Larson, H. Hammond, and C. Packard, Predicting long-term dark storage dye characteristics of color photographic products from short-term tests, J. Appl. Photography, 6, 42–45 (1980).
2. S. Anderson and R. Ellison, Natural Aging of Photographs, J. Am. Inst. Conserv., 31, 2, 213–223 (1992).
3. D. E. Bugner, C. Romano, G. A. Campbell, M. M. Oakland, R. Kapusniak, L. Aquino, and K. Maskasky, The Technology Behind the New Kodak Ultima Picture Paper—Beautiful Inkjet Prints that Last for Over 100 Years, IS&T's 13th Int. Symp. Photofinishing Technologies, 38–43 (2004). A downloadable file of this paper (pdf format) is available at: http://www.kodak.com/eknec/documents/63/0900688a801caf63/ULTIMAWhitePaper012804.pdf.
4. D. E. Bugner, J. LaBarca, J. Phillips, T. Kaltenbach, A. Bush, and J. Kapecki, Survey of Environmental Conditions Relative to Display of Photographs in Consumer Homes – Phase II, IS&T's Archiving Conf. Final Program and Proc., 179–183(2005)
5. Y. Kanazawa, Y. Seoka, S. Kishimoto, and N. Muro, Indoor Pollutant Gas Concentration and the Effect on Image Stability, IS&T's NIP20, 2004 Int. Conf. Digital Printing Technologies, 748–752(2004).

Author Biography

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