#### CORRELATION OF ACCELERATED LIGHTFASTNESS TESTING OF PAPER PRODUCTS WITH ACTUAL STOREROOM EXPOSURE

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Abstract: The lightfastness of printed and dyed paper products in a simulated storeroom was correlated to the results found in four accelerated fade instruments. The best correlation coefficients using color difference measurements was with the HPUV Indoor Actinic Exposure System. However overall instrument-storeroom correlations were only fair to poor. Correlations between instruments with different sources were generally good and were much better than the instrumentstoreroom correlations. This suggests that a good spectral match of irradiating sources, although necessary, is not sufficient to insure good accelerating aging correlations. Secondary factors in the instruments' testing significantly<br>changed the rank orders found in the storeroom. Analysis of changed the rank orders found in the storeroom. sample fade paths in CIELAB color space showed several examples where the instruments' paths diverged from the storeroom path.

#### Introduction

Much of the equipment available for lightfastness testing is designed to simulate accelerated weathering of paints and coatings exposed to exterior sunlight or sunlight filtered through a windowpane. The printing industry has often adopted the same equipment and testing procedures in evaluating the durability of pigments formulated into inks. The standard testing devices used to determine color permanency data in the NPIRI Raw Materials Data Handbook (Fetsko, 1983) are the carbon and xenon arcs. The Atlas (Fetsko, 1983) are the carbon and xenon arcs. Carbon Arc Fade-Ometer, first marketed in 1918, has a source unlike either daylight or any common indoor illumination source. The filtered Xenon Weather-Ometer was designed to simulate sunlight reaching the indoors. Currently the ASTM is revising its test method D3424, Standard Method of Evaluating the Lightfastness of Printed Matter. In that

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study the predominant sources remain the carbon arc and xenon arc testers. Some testing was done for the first time with the Atlas HPUV Indoor Actinic Exposure System which simulates cool white fluorescent light exposure.

In the social expression industry we want to ensure that our careful attention to accurate color reproduction of original artwork is not lost due to inappropriate choice of colorants which deteriorate on the shelf. The in-service environment for our products is the card shop lighted with cool white fluorescent bulbs. Therefore, we needed to determine which accelerated lightfastness tester best correlated with our retail store. In this study we compared color changes produced by four instruments to those changes found in a simulated retail store. We performed a detailed color analysis to determine if the different sources produced the same color changes seen in the storeroom. Our color comparisons went beyond computing the total color differences,  $\Delta E^*$ . We also compared the fade loci in three dimensional CIELAB color space for the samples irradiated by the different sources. Finally, we attempted to extract calibration factors relating the exposure in the instruments with real life exposure in our simulated card shop.

#### Experimental

Twelve samples, as shown in Table I, were chosen for this study. Three different media were represented: printing by gravure, by lithography and dyed paper stock (referred to as deco vellum). The colors printed by gravure were ivory, raspberry, scarlet and terra cotta. The samples printed by lithography were process colors of light cyan, magenta, pink and yellow. The deco vellum samples were in colors of denim blue, gypsy rose, raspberry and terra cotta. In each medium, representatives of both a lightfast and a fugitive nature were included.

#### Real Time Storeroom Fade Test

The storeroom where the real time test was conducted was windowless. Lighting in the room was provided with cool white deluxe fluorescent lamps. The level of lighting was adjusted to be approximately 80 footcandles in the center of the room at 44 inches above the floor. This measurement was representative of an average card shop. Using a timer, the lights were turned on at 9:00 am and off at 10:00 pm six days a week. Lights were turned off for the seventh day.

No provisions were made for temperature or humidity control in the storeroom. While the room was heated in the winter and air conditioned in the summer, it was subject to

the same seasonal fluctuations in temperature and relative humidity found in most commercial buildings.

The storeroom was furnished with fixtures commonly found in card shops: three variations of self-illuminated wall units; and a gondola and a card rack which were both illuminated by fluorescent ceiling lights. Specimens of each of the twelve colored samples were oriented vertically in the fixtures at the top, middle and bottom levels, just as displayed in a retail store. The one exception was the gondola which had a vertical display position at the bottom only. Four specimens of color were placed at the thirteen unique fixture positions. Samples were retrieved from the room every three months until the last sample set was exposed for one year.

#### Accelerated Fade Testing

Four accelerated fade instruments with different radiant sources were used for this part of the study. The sources included an enclosed carbon arc, a mercury vapor sunlamp, high output cool white fluorescent lamps and a xenon arc. Duplicate specimens were tested in each of the accelerated fade instruments for eight levels of continuous exposure.

Carbon arc exposure was tested in an Atlas FDAR Fade-Ometer. The globe was cleaned and the rods were changed every 24 hours. Though the black panel temperature was not recorded, the thermostatic temperature control was set at 90<sup>°</sup> F. Specimens were tested in this instrument from<br>5 to 40 machine hours in five hour increments. The 40 machine hours in five hour increments. The irradiance of the instrument was not controlled and was assumed to be constant.

Specimens exposed to the mercury vapor sunlamp were tested in a Hallmark Fade Tester D-0008 (similar to a Test Lab Apparatus Sunlighter II). This instrument consists of a mercury vapor sunlamp suspended above a rotating table to which specimens are attached. The specimens were tested from 5 to 40 machine hours in five hour increments. There was no temperature or humidity control, nor any control of the source irradiance, which was assumed to be constant.

Exposure to fluorescent lamps was accomplished in an Atlas HPUV Actinic Indoor Exposure System. The instrument exposed specimens to eleven super high output cool white bulbs for 2 to 16 Hewlett-Packard months, in intervals of two months. A Hewlett-Packard year is equivalent to the irradiation of 20,000  $w-h/m^2$  which was measured in business office environment. The irradiance measurements from the HPUV radiometer were used to calculate the exposure times to give Hewlett-Packard months. Although the temperature of the test chamber was not controlled, provisions were made to automatically shut off the instrument at temperatures in excess of 42 $^{\text{D}}$  C.

Specimens exposed to the xenon arc source were tested in an Atlas Ci65 Xenon Arc Weather-Ometer. The irradiance of the 6500 watt xenon lamp was controlled at 1.00  $W/m^2$ , at 420 nm. The inner filter used on the lamp was of borosilicate and the outer filter was of soda lime. The black panel temperature was 63 +/-  $3^{\circ}$  C and the relative humidity was 30  $+/-$  5%. Specimens were tested from 25 to 200  $\text{kJ/m}^2$  in increments of 25  $kJ/m^2$ .

#### Color Measurements

This yearlong storeroom experiment produced 648 samples for color measurement, while the instruments produced 768 samples. Color measurements were made with a Macbeth 1500+ Color-Eye which was interfaced to a Hewlett-Packard 86 computer. The instrument uses a pulsed xenon source with d/0 illumination. We used the small area view port with both specular light and ultraviolet irradiation included in the measurement. We wrote our own software to capture the reflectance values and to store them on disk with the sample identification and the computed CIELAB color values. Computations of  $L^*$ , a\* and  $b^*$  were performed for a D6500 source and the 10 degree standard observer per ASTM D-2244. Our own software reduced measurement cycles to only nine seconds per sample.

#### Rank Correlation from  $\Delta E^*$  Data

The extent of fade,  $\Delta E^*$ , was measured as the total color difference as computed in the following equation:

$$
\Delta E^* = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2}
$$
 (1)

The deltas preceding the CIELAB coordinates in (1) indicate differences between the unfaded and faded color values. The initial unfaded color coordinates were determined from an average of 64 samples. Table II shows the  $\Delta E^*$  results for all sample colors exposed to the five irradiance sources at four equally spaced exposure levels for each source. As noted in the experimental section, eight exposure levels were measured, but only half are reported here for the sake of brevity. The results from the storeroom are an average<br>of 10 of the 13 possible fixture positions. The top of 10 of the 13 possible fixture positions. positions of the self-illuminated fixtures are not in the calculations because they grossly exaggerated the average fade in the storeroom.

Figure 1 shows an example of the change of  $\Delta E^*$  as a ction of exposure in the Xenon Weather-Ometer. function of exposure in the Xenon Weather-Ometer. Surprisingly, most of the curves are linear with respect to exposure. Examination of similar curves for the other three instruments showed many nonlinear curves with both positive and negative concavity.  $\Delta E^*$ , the traditional measure of color change, is not proportional to pigment concentration as is the Kubelka-Munk K/S, the ratio of light absorbance to scattering (Grum and Bartleson, 1980). Even if  $\Delta E^*$  were proportional to concentration, one would only expect linear curves for zero order reaction kinetics. In a fade study of alizarin lake (Johnston-Feller, 1986) the classical kinetic rate law was first order and concentration was nonlinear with respect to exposure. The fact that we see linearity in  $\Delta E^*$  is remarkable in light of these considerations. It should be noted that there were very few crossovers of should be noted that there were very few crossovers curves in the AE\* diagrams. With the exposure levels chosen for each of the instruments we did not "burn out" all the color from any sample. Moreover, none of the colors quickly faded to an asymptotic plateau. Such cases would have caused problems in the rank order analysis because of many rank order crossovers at high irradiation levels.

Figures 2 and 3 show the relative responses of litho pink and gravure terra cotta to the five different types of<br>illuminants. Each of the bars in the clustered group Each of the bars in the clustered group represents the *L).E\** for one of the four exposure levels found in Table II. In comparing the two figures the response patterns are quite different, owing to the different wavelength sensitivities of the colorants. Examination of similar charts for the other ten color samples shows no two wavelength sensitivities alike. This phenomenon is well documented (Searle, 1984, 1987) for polymeric materials and printing inks. The different activation spectra of colorants caused different responses to the sources.

The data in Table II were then non-parametric statistic correlation coefficient: known as analyzed using the the Spearman rank

$$
r_{s} = \frac{\sum_{i} (R_{i} - R) (S_{i} - S)}{\sqrt{\sum_{i} (R_{i} - R)^{2}}^{1/2} (\sum_{i} (S_{i} - S)^{2})^{1/2}} \tag{2}
$$

where R<sub>i</sub> is the ranking of a sample according to the  $\Delta E^*$ under one irradiation source and  $S$ , is the same color's ranking under a second irradiation source. The bar over the variable indicates the mean rank for the source. Since we had five irradiation sources, a total of ten possible correlation coefficients can be computed for our data set. These were computed as seen in Table III for each of the<br>four exposure levels of the irradiator. The rank four exposure levels of the irradiator. The rank<br>correlation pairs were then averaged across the four correlation pairs were then averaged across the exposure levels. Entries in the table were then ranked by this average. With few exceptions the overall average gave the same ranking found in the individual exposure levels.

The instrument which best correlated with our simulated storeroom was the HPUV. This would be expected since both were illuminated by cool white fluorescent sources. Next in decreasing rank correlation came the Xenon Weather-Ometer, the Carbon Arc and finally the Sunlighter. Most surprising however is the poor correlation values found between the instruments and the storeroom. These could be judged fair at best. However, we found the Xenon and HPUV had the best interinstrument correlation. A .94 average coefficient between these instruments shows a very good agreement in the ranking of our twelve colored samples under accelerated testing. Yet the radiant energy distributions of the instruments' sources are quite different. In general, the instruments were better correlated with themselves than they were with the storeroom. The ran kings appear to be more a function of irradiance, power per unit area, than of source spectral energy distribution. Other variables in the accelerated testing may control the rate and course of the degradation. (Temperature and humidity are the first<br>variables which come to mind.) Besides this, storeroom variables which come to mind.) exposure was intermittent, whereas instrumental exposure was continuous.

Ideally accelerated testing affords an environment which maintains the same quantum yield for the photochemical degradation as in the service environment. It may be difficult to maintain the same chemical environment for the reactions due to diffusion limitations for reactants and products. Reactions could be slower in accelerated testing when insufficient oxygen can diffuse to the photoactivated molecules. Slow diffusion could concentrate acidic products<br>causing a catlytic increase in reaction rates with causing a catlytic increase<br>accelerated testing. With h With high intensity irradiation free-radical concentrations could reach such high levels that recombination to reactants might become a significant reaction pathway and quantum yield could be reduced. Any of these factors could have caused our samples to produce different rank orders under accelerated testing.

#### Fade Path Analysis

Thus far we have treated data only in terms of  $\triangle E^*$ . A basic assumption in this treatment is that the  $\Delta E^*$  found from irradiation by one source is equal to the same  $\Delta E^*$  for another source. Simply stated, it is assumed that they move<br>along the same locus in three dimensional color space. We along the same locus in three dimensional color space. wanted to test this assumption by plotting the coordinates of each colored sample under different irradiants in CIELAB<br>color space. Rather than just viewing scatterplots, we color space. Rather than just viewing scatterplots, developed equations which modeled the color path of the fading samples in CIELAB color space as a function of instrumental exposure. We found that the data could be adequately modeled by a simple polynomial of the third order.

$$
Y = a + bx + cx^{2} + dx^{3}
$$
 (3)

In equation (3) the Y represents one of the color coordinates,  $L^*$ ,  $a^*$  or  $b^*$ , and X represents exposure in the units of the storeroom or the accelerated testing of the storeroom or the accelerated testing instrument. The terms a through d are model coefficients determined by least squares. This was done for each color in each of the five sources. Nine points were available for each of the instrument-color combinations, eight exposure levels plus the starting point, but only five points were available for the samples from the storeroom. Color coordinates were averaged over all fixture positions to get the storeroom points for input into our program. The three equations needed to trace the fade path were later used to obtain the correlated exposure times of the storeroom samples in the lightfastness instruments.

Figures 4 and 5 show three dimensional plots of Gypsy Rose Deco Vellum. Figure 4 shows the storeroom path, Xenon and HPUV paths to be coincident within experimental error. However, in Figure 5 the fade loci for the Sunlighter and Carbon Arc diverge significantly from the storeroom. In viewing the paths of the entire set of colors we sometimes

found it difficult to decide whether the paths were the same or not. To be perceptibly different to the human eye  $\Delta E^*$ values normally must be greater than 2. When the uncertainty in the model path is also factored in, divergent<br>paths are not always significant in terms of human paths are not always significant in terms of perception. Charts were made of the actual faded samples. Three quarter inch discs were cut and placed on the vertical axis according to their computed  $\Delta E^*$ . The results from each source were plotted side by side in this manner. Samples of similar heights with different hues, confirmed a divergence in fade path. Several apparently divergent paths could not be corroborated visually. However divergent paths for the Sunlighter and/or Carbon Arc were verified for the colors litho pink, deco vellum gypsy rose, and gravure ivory. Overall we would have to say that the colors mostly followed the same paths as they did in the storeroom exposure.

#### Correlated Exposure Times

We next calculated the exposure time in each of the instruments which would best match the sample color from our storeroom. To do this we used the model equations described above. Given any exposure level we could calculate the three color coordinates for a sample fading in any lightfastness tester. Having the color coordinates of the storeroom sample and the coordinates of a point along the curve, we could calculate the distance, D, to the storeroom sample. As we mathematically moved along the curve we generated D as a function of instrument exposure. Thus we programmed a algorithm to find the instrument exposure which minimizes D for the sample point. All the samples were analyzed in this way and a file was built containing the exposure on each instrument and the distance of closest approach, D • Since some curves were definitely divergent, we rejected data where the D was greater than 2.0. We allowed some extrapolation,  $+12.5$ % of the exposure maximum, for storeroom samples that faded more than that found from the instruments. Table IV shows the correlated results. Each entry is an average over all fixture positions. Missing data indicates the paths were divergent or our moderate extrapolations were inadequate.

Figures 6-8 are samples of plots of instrumental exposure times correlated to actual storeroom months. The Xenon results show widely varying calibration slopes for different colors. The HPUV results are about the same when all colors are viewed. The data for the Sunlighter and Carbon Arc were much more scattered. Needing calibration factors we averaged the data across all colors for each three month interval and ran a least squares regression to give a best estimate calibration factor for each instrument. These data are shown in Figures 9-12. The tails indicate the one sigma limits for each point. On a relative basis the HPUV had a<br>smaller variance in the calibration factors. We were smaller variance in the calibration factors. surprised to see the sudden order out of chaos which appeared upon averaging the Xenon and HPUV data. The slopes are linear and pass through zero. The Carbon Arc and Sunlighter data showed a marked curvature due to artifacts<br>in data processing. Extrapolation should have proceeded Extrapolation should have proceeded further to give higher correlated exposures. we feel only the 3- and 6-months data are valid. A best slope was calculated from only these points. Table V shows our best estimate of instrument calibration factors from this analysis. The calibration factor derived for the HPUV shows that the irradiation in our card shops is only a third of that computed to simulate a business office.

#### Conclusions

The HPUV Indoor Actinic Exposure System correlated best with our simulated card shop. The Xenon Arc Weather-ometer was a very close second.

Instruments were better correlated with themselves than with the storeroom. Rank orders seemed more dependent on source intensity or other secondary instrumental variables than on spectral energy distributions.

Because of the different activation spectra of our colored samples, they showed different relative responses to the four sources for accelerated irradiation in this study.

Calibration factors relating instrument exposure with storeroom exposure varied widely by color. A simple universal calibration was not possible. Each color might have a different response to the increased irradiance of accelerated testing.

#### Acknowledgement

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Literature Cited

Fetsko, J • M. 1983. "NPIRI Raw Materials Handbook," Vol. IV, (NAPIM, Harrison, N.Y.), 368 pp.

Grurn, F. and Bartleson, c. J. 1980. "Optical Radiation Measurements," (Academic Press, New York), Vol. II, 372 pp.

Johnston-Feller, R. M

1986. "Reflections on the Phenomenon of Fading," Journal of Coatings Technology, vol. 58, no. 736, pp. 33-50.

Searle, N. D.

- 1984. "The Activation Spectrum and Its Significance to Weathering of Polymeric Materials," Atlas Sun Spots, vol 14, no. 33, pp. 1-4.
- 1987. "Printing Inks: Wavelength Sensitivities and Lightfastness Testing," Atlas Sun Spots, vol. 14, no. 38, pp. 1-4.

Color Samples Studied 12 Color - Media Combinations



# Table I







### CIELAB Delta E\*'s for all Samples in the fade Correlation Study Delta E\*'s were Measured from Unfaded Samples

Table II



CIELAB Delta E's for all Samples of Gravure Terra Cotta



CIELAB Delta E's for all Samples of Litho Process Pink

### **Spearman Rank Correlation Coefficients** Calculated from Delta E\* Data



**Table III** 



Fade Path of Gypsy Rose Deco Vellum



## **Correlated Exposure Time Averaged Over All Fixtures**









### **Table IV**















Storeroom Months Figure 12

# Correlated Exposure Factors



Table V