Further Studies on Reciprocity Effects for Accelerated Ozone Tests Compared to Ambient Air Exposure

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Abstract

The digital print industry is working toward the goal of adopting improved test methods for image permanence. This study focused on the impact of ozone concentration on the performance of inkjet print samples. Results from accelerated tests were compared to data collected from identical sample sets exposed to ambient air and to filtered air. Reciprocity failure was observed for some samples in the test, but the results also verified earlier work in which ambient air exposure can be generally linked to accelerated ozone test results. This research is part of ongoing work contributing to the development of standardized test methods for image permanence.

Introduction

About 5 years ago there was widespread investigation into predicting sample fade behavior due to ambient air. Thornberry and Looman made a strong case that ozone was the principal cause of inkjet sample fade in ambient air [1]. They also demonstrated a relationship between accelerated ozone testing and ambient air fade; however, in the second part of their experiment actual ambient ozone was approximated rather than measured directly and they acknowledged major sources of error including difference in the accelerated test environment compared to the ambient air—notably a much higher temperature.

Other papers attempted to correlate accelerated ozone testing to ambient air exposure, some showing reciprocity failures while others did not [2,3,4,5]. The presence of reciprocity failure, a difference between accelerated and ambient test results at equivalent exposures, appears to be a function of the samples tested, as some samples are not subject to reciprocity failure while others are.

The purpose of the research detailed in this paper was to apply recent learning involving dry time [6] and test temperature and test humidity [7] to minimize influence of variables that may affect conclusions derived from experimentation on the impact of ozone test concentration on sample fade rates and in comparing those results with ambient air exposure.

Experiment

The following equipment was used in the testing:

- Teledyne 400E UV Absorption O3 Analyzer
- Kahn Optidew Bench chilled mirror hygrometer
- SATRA/Hampden Model 903 ozone chamber
- Gretag Spectrolino/Spectroscan

A test cabinet similar to that described in [1] was also used. The cabinet was approximately 6 feet high with 4 inch openings on both sides near the floor containing fans pulling air into the cabinet that was then vented at the top. The vents were constructed as to minimize light exposure inside the cabinet. Specially designed wire shelving was used within the cabinet to minimize obstruction to airflow. Samples were hung by clips from the wire shelving. One cabinet was kept in the lab, where air was filtered for ozone, to be used as the control case. An identical cabinet was placed outside the lab, thereby allowing its samples to be exposed to ambient ozone.

All samples were printed at the same time to minimize variation due to printer setup or ink cartridges. The samples began testing within a few days of each other to minimize the effect of dry time (just over 2 weeks).

Accelerated ozone testing was done in the Hampden 903 chamber using a sample carousel that rotated samples within the chamber. The two test levels chosen were 0.5 PPM and 5 PPM ozone. The 0.5 PPM test started first and then was alternated with the 5 PPM test; however, the 5 PPM test finished much earlier as both targeted the same cumulative exposure levels: 10, 25, 100, and 250 PPM-hours. The accelerated tests were run at 23C/50%RH (+/-0.5C, +/-2%RH).

The ambient air test conducted outside the lab was within a large building best characterized as light manufacturing or warehouse storage. The ambient ozone was measured at 15 minute intervals throughout the test beginning in June and ending in September. Actual ozone levels varied from 0 to 28 ppb, generally following the amount of sunlight as shown in Figure 1. The average ozone level during the test was 10.75 ppb.

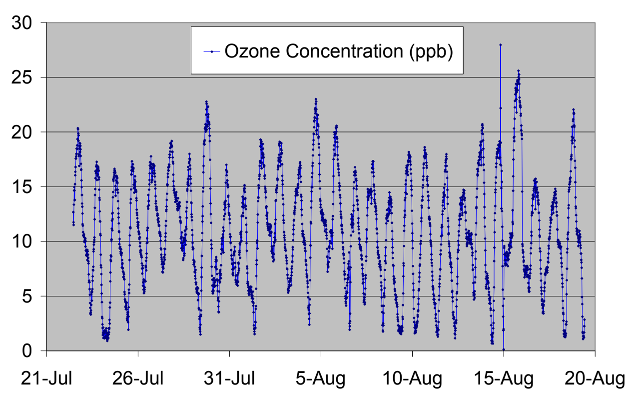

Figure 1. Ozone Measurements Collected During Ambient Ozone Test (in ppb). Four Week Window Shown is Representative of Entire Three Month Test.

The ambient temperature and relative humidity were also measured. The average temperature was 21C oscillating daily between 20-22C (min 19C, max 24C) and average humidity was 52% oscillating daily between 49-56% (min 44%, max 61%).

The lab temperature and humidity were kept at 23C/50%RH and varied by +/-1C and +/-3%RH. Although the ozone monitor is accurate to 1 ppb ozone, the air within the lab is scrubbed by eight 50 pound activated charcoal filters and the ozone monitor was not able to get an accurate reading (usually oscillating about zero). The ozone level in the lab was estimated to be about 0.3 ppb by comparing sample fade rates in the lab with the other test data.

Eight inks and seven media were selected for this study, for a total of 12 unique ink and media combinations. The inks included both dye and pigment, designated by letters. Media included both porous and coated matte papers, designated by numbers. Samples included density ramps of cyan, magenta, yellow, red, green, blue, and neutral color patches. From an initial density between 0.5 OD to 1.5 OD a patch was selected for each color that showed the greatest density change. In the comparative analysis, the same color patch was selected for all samples of a system across the various test conditions; so if the third cyan patch was selected on one sample at one ozone concentration, the same third patch on a matching sample was used for comparison at another ozone concentration. Measurement data shown is also an average from two sample replicates.

Results and Discussion

A large amount of data was collected in the experiment which necessitates the use of generalizations; however, where possible specific examples will be used.

The first general observation was that the paper white change was inconsistent between test conditions for many of the media. Some media yellowed as a function of test time while others yellowed according to ozone exposure. The net consequence is that because the density measurements do not correct for this change there is added noise in the measurements, particularly of light yellow ink patches.

The second general observation is that the ambient ozone test samples often faded slightly less than expected based on trends between the accelerated and lab control tests. One theory is that the slightly higher humidity in the ambient test resulted in more ink migration, thus increasing the patch density and making it measure as though it had not faded as much.

Table 1 shows data of System A1 comparing three tests at equivalent cumulative ozone exposure of 1 PPM-hours. This table demonstrates how the control ozone level was determined by matching fade rates. The outlier in this data set is the ambient yellow measurement, probably affected by humidity. This includes the yellow component (blue density) of the neutral, red, and green patches.

Table 2 shows System E3 using the same assumed lab ambient control ozone level as in Table 1. The outlier in this system is ambient magenta, also likely caused by humidity induced ink migration. This includes the magenta component (green density) of the neutral, red, and blue patches. The slight increase in yellow density loss at 0.5 PPM is due to less paper yellowing compared to the other test conditions (paper yellowing counteracts yellow ink fade in the measurements).

Table 3 compares fading of cyan patches in the accelerated ozone tests at 5 PPM and 0.5 PPM with the ambient ozone test all at the same cumulative ozone exposure of 25 PPM-hours. Media 2 and 4 shaded in gray were matte coated paper while all the others were porous photo papers. Ink B was a pigment ink while all the others were dye. Pigment inks such as the one in this test are not affected by humidity migration and it is interesting to note that it experienced the greatest deviation in fade rate between the accelerated and ambient ozone tests. System B1 showed a strong reciprocity failure between the 5 PPM and 0.5 PPM ozone test concentrations, which was consistent throughout the test. At a cumulative ozone exposure of 250 PPM-hours the cyan patches had faded 5.7% at 5 PPM and 10.7% at 0.5 PPM. However, the same ink on the coated media showed similar fade rates at 5 PPM and 0.5 PPM (i.e. no reciprocity failure).

Table 1. System A1 Density Change at 1 PPM-hours Cumulative Ozone Exposure.

Patch	Control	Ambient	0.5 PPM
Neutral	-9.0%	-8.7%	-10.0%
Neutral	-3.0%	-3.3%	-4.6%
Neutral	-3.2%	-0.3%	-1.8%
Cyan	-8.1%	-8.1%	-8.5%
Magenta	-2.5%	-2.6%	-4.0%
Yellow	-2.1%	0.7%	-3.2%
Red	-2.7%	-2.7%	-3.9%
Red	-3.8%	-0.9%	-3.6%
Green	-9.0%	-8.3%	-9.9%
Green	-1.9%	0.2%	-2.3%
Blue	-8.8%	-8.5%	-8.6%
Blue	-3.6%	-3.5%	-4.5%

Table 2. System E3 Density Change at 1 PPM-hours Cumulative Ozone Exposure.

Patch	Control	Ambient	0.5 PPM
Neutral	-8.1%	-7.2%	-8.3%
Neutral	-6.2%	-4.6%	-6.6%
Neutral	-1.8%	-1.4%	-3.1%
Cyan	-4.2%	-4.2%	-5.3%
Magenta	-5.4%	-3.6%	-5.0%
Yellow	-0.4%	-0.2%	-1.2%
Red	-5.0%	-4.3%	-5.7%
Red	-1.4%	-0.9%	-2.7%
Green	-8.4%	-7.9%	-9.4%
Green	-0.2%	-0.3%	-1.5%
Blue	-5.9%	-6.5%	-8.0%
Blue	-5.6%	-4.2%	-6.3%

Most ink media combinations in this test showed slightly more fade at 0.5 PPM than 5 PPM, while as mentioned earlier, ambient fading was usually less than this trend would have suggested. Yet when the data from all these systems are viewed as a whole it is remarkable how similar the ambient air fading is to the accelerated ozone testing at a common ozone exposure.

Table 3. Cyan Patch Density Change at 25 PPM-hours Cumulative Ozone Exposure.

System	5 PPM	0.5 PPM	Ambient
A1	-36.5%	-43.0%	-46.7%
A2	-14.2%	-15.6%	-14.8%
B1	-2.4%	-4.2%	-6.7%
B2	-2.5%	-2.9%	-6.2%
C3	-15.0%	-19.2%	-16.4%
C4	-8.1%	-9.0%	-8.3%
D3	-25.0%	-31.4%	-24.8%
E3	-30.5%	-35.4%	-27.1%
E4	-8.8%	-9.9%	-8.3%
F5	-9.9%	-11.6%	-10.4%
G6	-1.4%	-1.6%	-1.3%
H7	-9.1%	-10.9%	-10.4%

Table 4 shows results of the same test conditions for the magenta patches. Once again the 0.5 PPM test condition showed slightly more change than at 5 PPM. Magenta dye inks A, C, D, and E are known to be sensitive to humidity migration and all showed much less fading at the ambient test condition.

Table 4. Magenta Patch Density Change at 25 PPM-hours Cumulative Ozone Exposure.

System	5 PPM	0.5 PPM	Ambient
A1	-38.2%	-42.8%	-33.6%
A2	-22.2%	-25.7%	-18.8%
B1	-1.2%	-1.3%	-1.3%
B2	-1.5%	-1.4%	-1.7%
C3	-22.7%	-26.8%	-20.2%
C4	-19.2%	-21.0%	-18.2%
D3	-39.1%	-42.8%	-32.0%
E3	-53.0%	-54.2%	-39.7%
E4	-35.3%	-39.4%	-33.1%
F5	-3.3%	-4.0%	-2.1%
G6	-1.4%	-1.8%	-1.9%
H7	-8.5%	-9.5%	-9.5%

Table 5 shows density change of the yellow patches. The 0.5 PPM test again resulted in slightly more fading than at 5 PPM for most systems. Moreover, ambient fading continues to be less than expected. Ink migration remains the prime suspect, supported by the evidence of Ink A yellow which showed almost no fading at ambient and is also the most sensitive to humidity.

Table 5. Yellow Patch Density Change at 25 PPM-hours Cumulative Ozone Exposure.

System	5 PPM	0.5 PPM	Ambient
A1	-7.0%	-11.2%	0.4%
A2	-10.4%	-13.3%	-3.1%
B1	-0.6%	-0.8%	-0.5%
B2	-0.1%	-0.1%	0.1%
C3	-4.3%	-7.1%	-5.9%
C4	-4.1%	-5.5%	-5.8%
D3	-3.9%	-6.2%	-4.2%
E3	-3.1%	-5.0%	-2.3%
E4	-2.8%	-4.4%	-3.6%
F5	-11.5%	-14.1%	-7.2%
G6	-1.2%	-1.5%	-0.7%
H7	-14.0%	-16.8%	-11.5%

Trends seen between ozone test concentrations at one exposure level were generally the same as those seen at other exposure levels. For example, System G6 was one of the most robust systems tested in this experiment and variation seen at 25 PPM-hours is within the noise of measurement. However, as Figure 2 shows, the fade rate at a 0.5 PPM ozone concentration was about 40% greater than at 5 PPM throughout testing at multiple cumulative exposure levels.

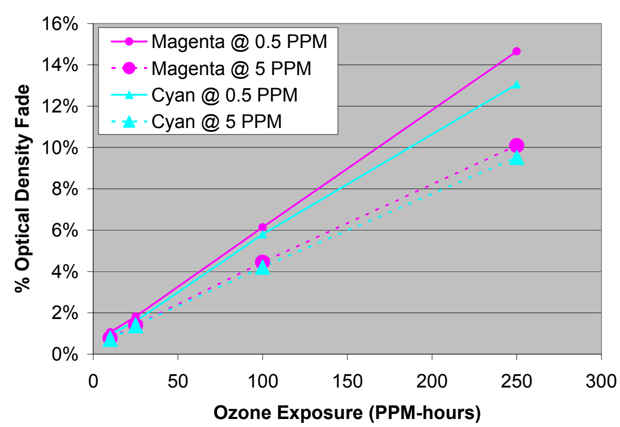

Figure 2. System G6 Cyan and Magenta Patch Fade For 0.5 PPM and 5 PPM Ozone Test Concentrations.

Up until now comparisons have been made via density change. However, another commonly employed method of comparing test results is to set a failure threshold and determine the time (or exposure) to failure. Figure 3 shows what happens when applying a 40% fade failure criteria to the cyan patches of Systems A1 and C3 run at 0.5 PPM and 5 PPM ozone concentration. Although each is fading about 20% more at equivalent ozone exposure at 0.5 PPM compared to 5 PPM, the time (or exposure) to reach the failure criteria takes 50% longer because of the nonlinear fade rate.

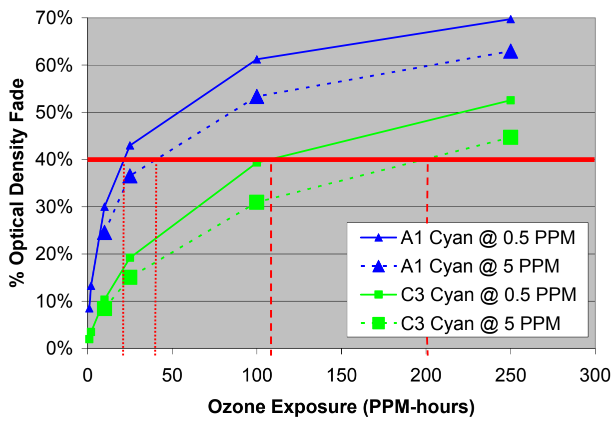

Figure 3. Systems A1 and C3 Cyan Patch Fade For 0.5 PPM and 5 PPM Ozone Test Concentrations.

Conclusion

This study minimized many factors that adversely influence ozone stability testing and thus achieved greater resolution in determining the impact of varying the ozone concentration on sample fading. This study also verified previous work that found accelerated ozone tests to be representative of ambient air fade.

However, it also found that most systems tested exhibited noticeable and consistent reciprocity failures between the two accelerated ozone test concentrations of 0.5 PPM and 5 PPM. In an effort to shorten the test length by applying higher ozone concentrations the results would unacceptably lead one to overpredict sample robustness. For one system studied, the fade rate was twice as great at the lower concentration for an equivalent ozone exposure level.

Previous studies have argued both for and against the presence of reciprocity failure in accelerated ozone testing. Based on data collected in this study, the significance of reciprocity failure depends entirely on the particular ink media systems investigated. For example, the ink that showed the greatest reciprocity failure on one media showed no reciprocity failure on another media. With current test methods, ink responses to ozone and to other environmental conditions are not separable from the ink media interactions with ozone and the environment. Therefore, the only way to ensure that reciprocity failure is not affecting the validity of the test results is to include reciprocity testing with every ink media system test.

Although accelerated ozone tests can provide a general approximation of ambient air fade, this investigation also showed that minor ambient environmental fluctuations can influence fade rates. For example, ink media systems which have been shown to fade more rapidly with higher humidity in accelerated testing measure as though less affected by ozone at higher humidity at ambient conditions. In an ambient condition, high humidity may occur during a low ozone level such that the impacts of humidity and ozone are independent, and vice versa. Designing a test with fluctuating ozone and humidity levels may more accurately reflect customer experience, but would be difficult to conduct and ensure repeatable results. Consequently, although accelerated ozone tests are useful for evaluating image permanence, the results of this study show that they are not reliable for predicting image life for a consumer. Therefore, until advances in test equipment make such testing practical, it is currently preferable to compare products as demonstrated in this paper—by presenting density change (or delta E) of different colors at a common ozone exposure level. Such a goal is achievable within the framework of a standardized test having controlled testing conditions.

References

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Author Biography

Matthew Comstock received his B.S and M.S. degrees from Purdue University in Mechanical Engineering specializing in heat transfer and thermodynamics. He joined Lexmark International, Inc. in 1999 as a development engineer for color laser products. Since 2005 he has been responsible for the Lexmark Image Permanence Lab in Lexington, KY. His work is primarily focused on image permanence test method development and image permanence testing.