Influence of Dry Time on Ozone Reciprocity Failure

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Abstract

Investigation into ozone testing has shown that print samples may be subject to ozone reciprocity failure. Many print samples in accelerated ozone testing fade faster at lower ozone concentrations in comparison to fade rates in tests run at higher concentrations to the same cumulative ozone exposures. In contrast to this trend, samples often faded more slowly in ambient air compared to the accelerated tests. Separate research had shown that ozone test results are sensitive to dry time, with longer drying typically improving image stability. This has implications for testing in ambient air, because the effective dry time of the print samples is increased due to the length of the test. This study focused on understanding how dry time may interact with ozone reciprocity failure and thereby explain the contrary trends observed.

Introduction

A study published last year investigated whether accelerated ozone tests could accurately predict performance in ambient air [1]. As part of that study, accelerated tests were run at two different ozone concentrations: 5 PPM and 0.5 PPM. Comparing the data at equivalent cumulative exposures found that many print systems faded more at the lower ozone concentration than at the higher level. However, that trend didn't hold as consistently when comparing to the ambient ozone exposure which averaged less than 11 ppb. Instead of fading more as would have been predicted from the accelerated tests, many samples faded less at ambient than in either of the accelerated tests.

At the time the paper was written it was thought that the slightly higher humidity in the ambient test had caused ink migration, thus increasing the optical density and negating part of the ozone fading. While a reasonable theory, and likely contributing to some of the observed behavior, it also fell short of fully explaining the data.

It was also known from prior research that ozone testing is highly susceptible to dry time, with longer dry times often improving the ozone stability of inkjet print samples [2]. The ambient test had taken over 3 months to finish, while the accelerated tests only took a few weeks to complete. In effect, the samples in the ambient test were still 'drying' before receiving enough ozone exposure to significantly fade the samples, thus the 'effective dry time' of the ambient test was much longer than the accelerated tests. Could this longer 'effective dry time' be responsible for the lower fade rates observed in the ambient test? This paper investigates these interactions and whether longer dry times can alter the conclusions drawn from ozone reciprocity testing.

Experiment

The method of studying the influence of dry time on ozone reciprocity failure was nearly identical to the previous study. As before, all samples were printed at the same time. From these samples the following tests were run:

- 5 PPM ozone testing with 2-week dry time
- 0.5 PPM ozone testing with 2-week dry time
- ambient air testing with 2-week dry time
- 5 PPM ozone testing with 6-week dry time
- 0.5 PPM ozone testing with 6-week dry time

The ambient air test was comparable to the previous year's test except the average ozone level was 8.5 ppb and required just over 4 months to complete.

The 5 PPM and 0.5 PPM tests were started within a day of each other and each test alternated time in the test chamber at their respective ozone concentrations. This approach minimized any difference in dry time between the accelerated tests while using samples that had all been prepared at the same time.

Test samples were evaluated from 12 unique systems, and most are different from those investigated in the previous study. Inks are identified by the letters A through P and media by the numbers 1 through 5. Pigment and dye based inks were printed on porous photo papers recommended by their respective manufacturers.

Results and Discussion

As in the previous study, the results will be compared at the same cumulative ozone exposure of 25 PPM-hours. Table 1 shows cyan patch density change from each of the three ozone tests with a 2-week dry time. The first observation is that the fade rate at 5 PPM is less than the fade rate at 0.5 PPM for all the systems tested. Three of the four pigment ink systems, shown with grayed cells, could be argued to have equivalent fade based just on this data; however, a comparison at 250 PPM-hours shown in Table 2 reveals an increasing gap between the fade rates. This reciprocity failure between 5 PPM and 0.5 PPM ozone for cyan patches agrees with data collected in the previous study.

Table 1. Cyan patch density change at 25 PPM-hours cumulative ozone exposure with 2-week dry time for all tests.

Cyan	25 PPM-hours		
System	5 PPM	0.5 PPM	Ambient
A1	-37.4%	-41.2%	-39.5%
B1	-2.8%	-3.2%	-4.4%
C1	-5.7%	-6.6%	-10.0%
D1	-20.7%	-22.7%	-18.4%
E2	-2.8%	-3.1%	-4.5%
F2	-36.0%	-40.3%	-32.3%
G2	-6.1%	-6.7%	-4.8%
H3	-7.1%	-8.9%	-7.1%
J4	-8.9%	-10.7%	-5.7%
K5	-1.5%	-2.1%	-1.0%
M5	-2.8%	-2.9%	-3.8%
P4	-3.7%	-4.2%	-2.0%

The second observation from Table 1 is that for pigment inks the fade rate in ambient air continues the inverse relationship trend (increasing fade with decreasing concentration) seen between the 5PPM and 0.5 PPM tests. The data from the previous study did not reveal such a stark contrast as it only included one pigment ink. The previous study had also suggested that ink migration due to higher humidity in the ambient air test was responsible for less fading. Given that pigment inks are not affected by humidity migration, the data here would support that theory—except that cyan dye inks are also not generally susceptible to ink migration.

Table 2. Cyan patch density change at 250 PPM-hours cumulative ozone exposure.

Cyan	250 PPM-hours	
System	5 PPM	0.5 PPM
A1	-63.5%	-68.2%
B1	-6.4%	-7.6%
C1	-14.4%	-17.0%
D1	-44.8%	-48.2%
E2	-8.6%	-10.1%
F2	-64.9%	-69.8%
G2	-18.4%	-20.7%
H3	-23.1%	-30.5%
J4	-31.8%	-37.5%
K5	-8.5%	-12.4%
M5	-6.9%	-8.3%
P4	-14.3%	-19.4%

To examine whether dry time alters the reciprocity relationship, Table 3 substitutes in the 6-week dry time accelerated test data in place of the 2-week dry time data. As expected, the samples in the accelerated tests faded less with longer dry time. This amplified the reciprocity failure for the pigment ink systems when compared with the ambient air results. It also changed the observed reciprocity trends for some of the dye ink systems. For example, system A1 ambient air fade had originally been between the levels observed from the 5 PPM and 0.5 PPM tests, but when the dry time was extended to 6 weeks the ambient air fade result is much greater than either accelerated test. The trend reversal is not as apparent for systems such as G2, which went from much less fading in ambient air to about the same level of fading in ambient air as compared to the accelerated tests. One possible reason for this outcome is that the 6-week dry time for the accelerated tests was insufficient to match the effective dry time of the ambient air test. Yet there is one further explanation as to why the ambient air fade may still be the same or less than the accelerated tests. The average temperature of the ambient air test was 21.4C, which was less than the average temperature of the accelerated tests at 23C. It is known from previous work that ozone fading can be significantly reduced with a temperature that is 4C colder [3]. What is not known is the sensitivity of the ozone fading of these inks to the narrower temperature difference in this testing.

Table 3. Cyan patch density change at 25 PPM-hours cumulative ozone exposure with 6-week dry time for accelerated tests.

Cyan	25 PPM-hours		
System	5 PPM	0.5 PPM	Ambient
A1	-31.9%	-33.7%	-39.5%
B1	-1.8%	-2.3%	-4.4%
C1	-4.6%	-5.1%	-10.0%
D1	-17.3%	-18.8%	-18.4%
E2	-2.7%	-2.9%	-4.5%
F2	-28.8%	-30.7%	-32.3%
G2	-4.8%	-5.3%	-4.8%
H3	-7.0%	-7.5%	-7.1%
J4	-8.8%	-10.4%	-5.7%
K5	-1.4%	-1.7%	-1.0%
M5	-2.4%	-2.7%	-3.8%
P4	-3.5%	-3.9%	-2.0%

The magenta patch density change for the three ozone tests having a 2-week dry time is shown in Table 4. In contrast to the cyan inks, at 25 PPM-hours of ozone exposure only half of the magenta inks show any discernible reciprocity failure between the 5 and 0.5 PPM ozone concentrations. However, when this is extended to 250 PPM-hours of ozone exposure, as shown in Table 5, then reciprocity failure is observed in all but two of the systems. Special note should be taken of system F2, which at 250 PPM-hours had nearly faded to white. Although the density change at this exposure was comparable for the two ozone levels, it was fading faster at 0.5 PPM during an earlier part of the test. This illustrates the futility of attempting to draw distinctions between two test patches that have both faded more than 60%—all samples will eventually fade to paper white after enough ozone exposure. Also in contrast to the cyan pigment inks, only one of the magenta pigments inks, system E2, is showing slightly greater ambient air fade than the accelerated tests.

Table 4. Magenta patch density change at 25 PPM-hours cumulative ozone exposure with 2-week dry time for all tests.

Magenta	25 PPM-hours		
System	5 PPM	0.5 PPM	Ambient
A1	-33.4%	-36.0%	-26.8%
B1	-1.8%	-1.9%	-0.4%
C1	-4.3%	-4.5%	-4.2%
D1	-9.5%	-10.7%	-7.4%
E2	-1.9%	-1.7%	-2.4%
F2	-45.0%	-48.1%	-34.1%
G2	-1.9%	-1.9%	-1.2%
H3	-2.5%	-2.5%	-2.4%
J4	-2.7%	-3.0%	-1.2%
K5	-1.2%	-1.7%	-1.3%
M5	-3.9%	-4.0%	-3.7%
P4	-1.7%	-2.0%	-0.9%

Table 5. Magenta patch density change at 250 PPM-hours cumulative ozone exposure.

Magenta	250 PPM-hours	
System	5 PPM	0.5 PPM
A1	-73.5%	-76.1%
B1	-3.8%	-4.3%
C1	-9.0%	-9.5%
D1	-40.7%	-44.2%
E2	-6.0%	-6.1%
F2	*-81.8%*	*-81.8%*
G2	-12.8%	-13.7%
H3	-13.0%	-14.1%
J4	-18.7%	-20.9%
K5	-8.8%	-12.1%
M5	-7.6%	-8.5%
P4	-9.8%	-11.6%

To see whether dry time impacts magenta inks in the same way that it affects the cyan inks, the 6-week dry time accelerated test results are compared to the ambient air test data in Table 6. Once again the longer dry time resulted in a reduction in the ozone fade rates of many of the accelerated test samples, but the magnitude of the reduction was insufficient to achieve a reversal in some of the ozone reciprocity trends observed earlier. The C1 system is one case in which, with the extended dry time in the accelerated tests, the ambient condition resulted in significantly more fade. The two systems with the largest deviation between ambient air and accelerated tests, A1 and F2, also happen to be most sensitive to humidity. These systems showed a density increase of 13.9% and 9.4%, respectively, when exposed at 25C/85%RH for 3 days. The lower average ambient air temperature may explain the rest of the discrepancy from the accelerated tests.

Table 6. Magenta patch density change at 25 PPM-hours cumulative ozone exposure with 6-week dry time for accelerated tests.

Magenta	25 PPM-hours		
System	5 PPM	0.5 PPM	Ambient
A1	-29.6%	-30.7%	-26.8%
B1	-1.1%	-0.9%	-0.4%
C1	-2.5%	-2.5%	-4.2%
D1	-8.6%	-9.0%	-7.4%
E2	-2.0%	-1.8%	-2.4%
F2	-39.2%	-40.8%	-34.1%
G2	-1.6%	-1.8%	-1.2%
H3	-2.0%	-1.9%	-2.4%
J4	-2.6%	-2.6%	-1.2%
K5	-1.5%	-1.5%	-1.3%
M5	-3.5%	-3.4%	-3.7%
P4	-1.6%	-1.6%	-0.9%

The yellow patch density change for the three ozone tests having a 2-week dry time is shown in Table 7. In general the yellow inks were much more stable in ozone and trends between the accelerated tests are hard to detect at 25 PPM-hours of ozone exposure. The yellow ink ambient air data deviates from the accelerated tests far more than the other ink colorants. Two of the pigment ink colorants, B1 and C1, showed greater density at the end of the test in the ambient condition than at the beginning. This cannot be explained by humidity or by paper yellowing for these systems.

Table 7. Yellow patch density change at 25 PPM-hours cumulative ozone exposure with 2-week dry time for all tests.

Yellow	25 PPM-hours		
System	5 PPM	0.5 PPM	Ambient
A1	-10.0%	-7.6%	-0.3%
B1	-0.9%	-1.1%	1.6%
C1	-1.3%	-1.1%	1.6%
D1	-7.1%	-7.3%	-3.3%
E2	-1.0%	-1.0%	-0.4%
F2	-11.2%	-11.7%	-6.0%
G2	-2.0%	-2.2%	-0.9%
H3	-1.7%	-2.0%	-1.2%
J4	-11.2%	-12.8%	-5.1%
K5	-0.7%	-1.0%	-0.2%
M5	-0.2%	-0.2%	-0.5%
P4	-2.6%	-3.0%	-1.5%

Extending the ozone exposure to 250 PPM-hours, as shown in Table 8, reveals that half of the systems faded more at an ozone level of 0.5 PPM than at 5 PPM.

Table 8. Yellow patch density change at 250 PPM-hours cumulative ozone exposure.

Yellow	250 PPM-hours	
System	5 PPM	0.5 PPM
A1	-41.4%	-41.2%
B1	-2.1%	-2.4%
C1	-2.7%	-2.4%
D1	-30.5%	-32.0%
E2	-2.8%	-2.6%
F2	-41.2%	-41.3%
G2	-17.2%	-19.1%
H3	-10.1%	-11.2%
J4	-41.2%	-48.5%
K5	-4.2%	-5.1%
M5	-0.7%	-0.5%
P4	-12.8%	-15.2%

The yellow ink accelerated test data having a 6-week dry time is compared with the ambient air fade data in Table 9. Even with the reduced fading at the longer dry time, the ambient air data is still fading less than the accelerated tests for most of the ink systems. It is known that if systems A1, D1, F2, H3, J4 and P4 are exposed to high humidity that their density can increase enough to obscure any ozone reciprocity trends for this ambient air test. The humidity sensitivity of G2 and K5 are unknown; B1, C1 and E2 are not sensitive to humidity. Likewise, as with the other colorants, the lower average temperature of the ambient air test may be a factor.

Table 9. Yellow patch density change at 25 PPM-hours cumulative ozone exposure with 6-week dry time for accelerated tests.

Yellow	25 PPM-hours		
System	5 PPM	0.5 PPM	Ambient
A1	-7.5%	-7.5%	-0.3%
B1	-0.5%	-0.6%	1.6%
C1	-0.5%	-0.4%	1.6%
D1	-5.4%	-5.9%	-3.3%
E2	-0.9%	-0.9%	-0.4%
F2	-6.8%	-7.7%	-6.0%
G2	-1.4%	-1.7%	-0.9%
H3	-1.2%	-1.1%	-1.2%
J4	-10.3%	-11.8%	-5.1%
K5	-0.9%	-1.1%	-0.2%
M5	-0.1%	-0.1%	-0.5%
P4	-2.3%	-2.8%	-1.5%

Conclusion

A trend often observed during accelerated ozone testing is that fading increases when the ozone test concentration is decreased for the same cumulative ozone exposure. However, the ambient air test often showed less fading than the accelerated tests, thereby not following the same trend set forth by the accelerated tests.

The purpose of this study was to determine if dry time can influence the conclusions drawn from ozone reciprocity testing because of the extremely long test times required for testing at low ozone concentrations. It was found that many print samples faded less in ozone by increasing the dry time of the accelerated tests from 2 weeks to 6 weeks. This reduction in ozone fading brought the ambient air data into closer alignment with the observed trends between accelerated tests at different ozone concentrations. Thus dry time can alter the conclusions made from reciprocity testing. Unfortunately this adjustment was not sufficient to resolve all of the discrepancies between the accelerated tests and the ambient tests.

Among the systems tested, the reciprocity failure trends were most easily detected with cyan inks, especially the cyan pigment inks. Moreover, increasing the dry time resulted in exceptionally consistent data trends between the ozone test concentrations as shown in Table 3. The magenta and yellow ink colorants had more systems where the ambient air fade data was not consistent with the accelerated test data. Some of these cases may be caused by humidity induced ink migration while the remainder may be from the lower test temperature of the ambient air fade. Further work is needed to quantify this impact.

References

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Author Biographies

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.

Ann McCarthy is an Imaging Systems Architect with Lexmark International, Inc., in Lexington, KY. She received her BS (1982) in Computer Engineering and MS (1997) in Imaging Science from the Rochester Institute of Technology. Ms. McCarthy has been active in the imaging and printing industry for over 25 years, including seventeen years with Eastman Kodak Co., five years with Xerox Corporation, and over five years with Lexmark International, Inc., with contributions in color image and print path development, color data encoding, imaging interoperability across distributed workflows, and work on related international standards, including IEC ISO JTC1 SC28, CIE Div 8, ISO TC 42, ECMA TC46, and the International Color Consortium (ICC). Her publications include IS&T tutorials on color management, ICC white papers, and ISCC, SPIE and IS&T conference presentations.