Effect of Temperature and Humidity on Rate of Image Fading in Ozone

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Abstract

The digital print industry is working toward the goal of adopting improved test methods for image permanence. As part of this effort, the new test methods are being designed to isolate the environmental variables that impact image permanence. The benefits of this approach are that it simplifies the test method and test equipment while promoting test results that can be reproduced at other test laboratories. This study focused on the impact of varying the temperature and humidity during ozone stability tests while keeping all other known variables constant. The data is useful for evaluating acceptable tolerances for temperature and humidity to achieve consistent results during an ozone stability test. This research is part of ongoing work contributing to the development of standardized test methods for image permanence.

Introduction

Durability of printed images is assessed through a variety of image permanence tests. This study examined the impact of variation in humidity and temperature in a test method used to determine the influence of ozone on printed images. There are several known air contaminants which react with printed images and can cause them to fade over time [1]. The test method applied here focuses on ozone, since its contribution to sample fade (relative to other contaminants) is often the largest.

Lexmark recently purchased a SATRA/Hampden ozone chamber model 903 to add to our existing MAST/Lunaire ozone chamber. The 903 uses a closed air loop cycle while the MAST uses an open air loop. Both chambers were modified in the Lexmark lab to improve airflow, ozone, temperature, and relative humidity uniformity both spatially and over time.

Table 1. Data Comparing Fade Rates of Two Inks Between Hampden 903 and MAST/Lunaire Ozone Chambers.

	Cyan OD Loss		Magenta OD Loss	
	903	MAST	903	MAST
Ink 1	10.5%	9.7%	7.2%	6.8%
Ink 2	47.6%	47.3%	55.0%	55.5%

Table 1 shows a summary of the data collected during the qualification of the new ozone chamber. The actual difference in optical density loss was 0.5%. Although ozone exposure, temperature and humidity were equal during these tests, the air flow rate and the air flow cycle were different. Separate tests show that air flow can affect the ozone fade rate [2]; however, given the closeness of this data, it is unlikely that open or closed air loop had any effect.

The data in Table 1 omits the fact that there was a larger variation between some replicates within the Hampden 903 ozone chamber itself as shown in Table 2. During the qualification, samples were mounted at high and low positions on a rotating carousel. The carousel ensured that all samples saw the same average X-Y plane conditions over time, however there was no motion in the Z-axis. Earlier measurements had found that there was a slight temperature variation within the chamber in the Z-axis: 22.6C in the high position and 23.4C in the low position, the samples were separated by a distance of 15cm.

Table 2. Data Comparing Fade Rates of Two Inks Based on Sample Position in Hampden 903 Ozone Chamber.

	Cyan OD Loss		Magenta OD Loss	
	High	Low	High	Low
Ink 1	10.3%	10.8%	7.0%	7.4%
Ink 2	48.6%	46.6%	55.9%	54.1%

Environmental variations such as these are common in many test chambers, and are often larger than this. Particularly troubling was the magnitude of the sample's potential response to this small change in environment, which is well within typical ozone test method tolerances. To determine whether the data in Table 2 indicated a repeatable test method outcome due to environment, a series of experiments were designed to quantify the actual effect of temperature and humidity on the ozone fade rate of a variety of inks and media.

Experiment

The following equipment was used in the ozone testing:

- Teledyne 400E UV Absorption O3 Analyzer
- Lunaire CEO 910W-4 environmental chamber
- MAST Keystone Ozone Generator 700-10LTA
- Kahn Optidew Bench chilled mirror hygrometer
- Testo 445 hot bulb anemometer
- Gretag Spectrolino/Spectroscan

The ozone fade testing was run exclusively in the MAST/Lunaire chamber because its hybrid design was more suited to changing environmental conditions. The MAST ozone generator feeds ozonized air into the Lunaire environmental chamber, which is capable of reaching extreme temperature and humidity conditions.

For the testing, fresh samples were used at each environmental condition. A total of 9 environmental conditions were tested, with each test lasting 20 hours at an ozone concentration of 5 parts per million. All test samples were printed on the same day using 9 commercially available printers and 7 commercially available media. Since separate experimentation showed that dry time affects the ozone fade rate [2], the samples were allowed to dry 6 weeks in an ozone free environment before the first test began. The incremental effect of drying 6 to 8 weeks is smaller than between 2 to 4 weeks.

To further reduce noise in the test, the test target was designed with 45 magenta patches of identical density and 45 cyan patches of identical density as shown in Figure 1. Yellow was not used as it is not usually the first color to fail in an ozone test. Two sample replicates were tested for each system, so that 90 patches were averaged together in the analysis.

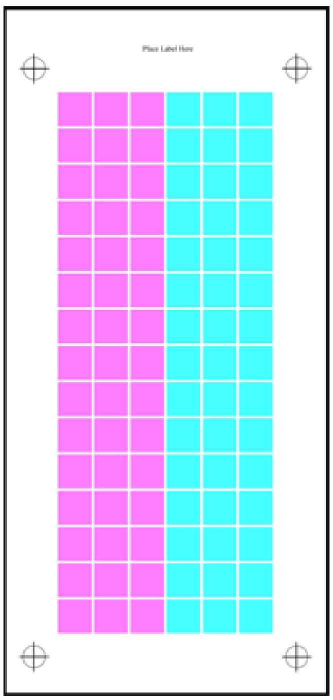

***Figure 1**. Test Target (90 blocks, Light Magenta on Left and Cyan on Right)*

A majority of samples showed consistent fade rates across all 45 patches. Data from the most erratic printer is shown in Table 3. The lower fade rate across the top patches—and to a lesser extent the ones along the outside edge—occurred regardless of the sample orientation within the chamber. Those patches had a slightly lower initial optical density and a slightly higher final optical density. Therefore variation in the jetting of the ink may be responsible for the variation in fade rate. Although this variation did not occur with most printers, it demonstrates the importance of multiple patches at different locations to get an accurate representation of a print system.

Table 3. Data from Cyan Patches of Single Test Target with Ink 5 Media C Run at 23C/50% and 5 ppm Ozone for 20 Hours.

% OD Loss (individual patches)		
-35.1%	-35.1%	-34.5%
-37.2%	-37.2%	-36.3%
-38.0%	-38.0%	-36.8%
-38.6%	-38.6%	-37.2%
-38.8%	-38.8%	-37.3%
-38.8%	-39.0%	-37.5%
-39.3%	-39.2%	-37.6%
-39.4%	-39.3%	-37.7%
-39.4%	-39.2%	-37.8%
-39.5%	-39.4%	-38.0%
-39.5%	-39.4%	-37.9%
-39.6%	-39.4%	-38.1%
-39.9%	-39.8%	-38.2%
-40.0%	-39.9%	-38.5%
-39.9%	-39.8%	-38.4%

Due to the limited time to run 9 environmental tests sequentially in a single ozone chamber, dye based inks were selected for testing on porous photo papers. The one exception to this was Ink 1, in which a dilute pigment photo ink was tested. Pigment inks are generally more ozone resistant than dye based inks; however, a dilute pigment ink as may be found in photo cartridges may fade faster than a non-dilute pigment ink of the same color.

It is standard practice in Lexmark's image permanence lab to calibrate all temperature and humidity sensors to a single reference chilled mirror hygrometer. Moreover, each test chamber has a second set of temperature and humidity sensors that log data to a central database. For this testing a third set of sensors was added to monitor conditions at the sample. Because all tests were run in the same chamber over a short period of time, the effect of sensor drift and calibration error between equipment was minimized. The actual chamber set points were close enough together to reduce the effect of sensor nonlinearity, which shows up in the wider operating ranges of the humidity and thermal stability tests.

Results and Discussion

The first test run was performed at the nominal test conditions of 23C and 50% relative humidity. The test concentration and length resulted in a cumulative ozone exposure of 100 ppm-hours. This level of exposure would be reached in about 1 to 2 years of ambient exposure.

As can be seen in Table 4, the ozone stability of the inks and media varied widely.

Table 4. Data from Test Run at 23C/50% and 5 ppm Ozone for 20 Hours.

		Cyan % OD Loss	Magenta % OD Loss
Ink 1	Media A	8.3%	2.5%
Ink 1	Media B	5.7%	2.6%
Ink 2	Media A	44.5%	52.3%
Ink 2	Media B	56.4%	66.1%
Ink 3	Media C	21.6%	34.9%
Ink 4	Media C	37.4%	50.0%
Ink 5	Media C	38.8%	77.6%
Ink 6	Media D	17.4%	13.3%
Ink 7	Media E	34.2%	31.3%
Ink 7	Media F	33.8%	39.9%
Ink 8	Media E	17.5%	8.0%
Ink 8	Media F	16.2%	12.8%
Ink 9	Media G	4.5%	4.3%

Subsequent test runs evaluated the effects of limited variations in humidity and temperature. Table 5 shows test results from testing at 4C and 5% relative humidity below and above the nominal test condition. Results are shown relative to the results from the 23C/50% nominal test environment. All tests were conducted with the same test concentration and length resulting in a cumulative ozone exposure of 100 ppm-hours.

Table 5. Comparing Data from Tests Run at 19C/45% and 27C/55% with the Previous Test Run at 23C/50%.

	Cyan Deviation from 23C/50%		Magenta Deviation from 23C/50%	
System	19C/45%	27C/55%	19C/45%	27C/55%
1A	-17.4%	22.0%	-8.4%	30.3%
1B	-11.8%	14.7%	-9.1%	24.6%
2A	-19.6%	34.2%	-18.2%	31.4%
2B	-14.8%	16.2%	-12.6%	14.4%
3C	-31.9%	87.5%	-28.0%	59.0%
4C	-26.2%	45.6%	-21.4%	35.4%
5C	-26.8%	29.4%	-14.3%	10.4%
6D	-16.5%	21.6%	-8.9%	20.0%
7E	-19.2%	26.7%	-17.2%	25.9%
7F	-11.4%	17.8%	-6.5%	14.5%
8E	-21.0%	25.0%	-21.3%	19.9%
8F	-20.6%	19.6%	-16.5%	9.0%
9G	-22.6%	54.2%	-19.3%	42.4%

At lower temperature and relative humidity all systems faded slower than the nominal test condition. Likewise, at higher temperature and relative humidity all systems faded faster.

To separate out the effect of temperature and humidity on this response, further tests focused on only changing one parameter at a time.

Based on data shown in Table 6, simply changing the temperature while keeping relative humidity constant yielded some unexpected results. While all systems showed faster fading at higher temperature, not all systems showed slower fading at lower temperature.

In looking over the sensor logs it was found that during each 19C test run—at about 12 hours into the 20 hour test—there was a short spike in temperature and humidity. The temperature rose to about 23C and the humidity nearly reached saturation for about 10 to 15 minutes. It is therefore likely that the samples which faded more at 19C than at 23C were sensitive to humidity. The behavior of the chamber is indicative of a defrost cycle, and it is unusual in that it appears to be on a timer and only activated below a particular temperature—as it was not seen at 23C or higher test temperatures. This unexpected test result illustrates the importance of closely monitoring the test conditions and the need for a test method to specify both an average test condition and limits for dynamic fluctuations during the test.

Table 6. Comparing Data from Tests Run at 19C/50% and 27C/50% with the Nominal Test Run at 23C/50%.

	Cyan Deviation from 23C/50%		Magenta Deviation from 23C/50%	
System	19C/50%	27C/50%	19C/50%	27C/50%
1A	-14.8%	7.9%	-1.6%	20.1%
1B	-12.3%	7.2%	-8.5%	8.3%
2A	11.2%	8.6%	1.2%	9.5%
2B	-0.2%	4.2%	-3.2%	5.1%
3C	38.4%	22.8%	9.4%	13.7%
4C	8.2%	11.4%	-2.8%	9.0%
5C	-11.0%	8.8%	-8.5%	3.0%
6D	-4.3%	14.5%	-11.7%	13.8%
7E	-0.2%	7.2%	-7.8%	12.8%
7F	-2.3%	10.7%	-4.3%	12.0%
8E	-8.3%	10.3%	-14.8%	11.0%
8F	-15.5%	7.1%	-16.4%	3.0%
9G	-18.4%	23.0%	-9.5%	18.4%

Table 7 shows the effect of relative humidity on ozone fade. As deduced from the previous unexpected test results, higher humidity does accelerate the ozone fade rate of nearly all systems; in particular those systems (e.g. Ink 3 / Media C) affected by the humidity spike in the 19C tests. Overall, a 5% change in humidity had a stronger effect on more systems than a 4C change in test temperature. The only unexpected test result was from the magenta ink of system 8F, which faded slower at both lower and higher humidity. The ozone fade rate often responded nonlinearly to humidity as demonstrated by additional data shown in Tables 8 and 9 in the Appendix.

Table 7. Comparing Data from Tests Run at 23C/45% and 23C/55% with the Nominal Test Run at 23C/50%.

	Cyan Deviation from 23C/50%		Magenta Deviation from 23C/50%	
System	23C/45%	23C/55%	23C/45%	23C/55%
1A	-5.2%	5.6%	-1.3%	19.8%
1B	-7.0%	0.9%	-9.1%	-0.5%
2A	-7.2%	15.9%	-4.7%	14.0%
2B	-9.3%	7.5%	-5.8%	4.9%
3C	0.4%	38.9%	-1.3%	31.3%
4C	-8.7%	20.4%	-6.5%	17.1%
5C	-17.4%	12.2%	-9.3%	4.9%
6D	-5.7%	5.9%	0.1%	2.8%
7E	-12.4%	14.5%	-4.4%	8.4%
7F	-5.5%	9.3%	1.4%	6.4%
8E	-11.1%	12.0%	-7.5%	1.7%
8F	-9.8%	2.1%	-5.9%	-11.0%
9G	-6.6%	10.3%	2.5%	8.6%

Referring back to the data shown in Table 2, the variation in fade rates seen from a high and low mounting position can be explained by the small environmental difference between those locations. A 0.8C temperature difference also causes a 2.4% change in relative humidity within the closed space of the test chamber (constant dewpoint). The higher mounting position was slightly colder and therefore would have a higher relative humidity. Ink 1 was shown to be affected more by temperature than by humidity, and it faded more at the lower mounting position (higher temperature). Ink 2 was shown to be affected more by humidity, and it faded more at the high position (higher humidity).

Conclusion

Based on the collected test data, the decision was made to only mount samples in the middle of the Hampden 903 ozone chamber. This effectively cut the sample capacity in half, but ensured that consistent test data would be collected.

Due to the logistical and resource demands of testing at different environmental conditions, it was not possible to run a traditional test with multiple measurements of a sample over a period of time. Typically in an ozone test, the fade rate begins to slow down over time and results in large differences in failure times with only small variations in the actual optical density loss. This is further compounded by the color imbalance calculations themselves, which can react strongly to different environmental test conditions—one environment may cause a color imbalance while another simply does not, as opposed to merely delaying it. This has been observed during the past few years as general ozone test conditions have changed from 24C/60% relative humidity to 23C/50%. Some systems were found to have an estimated color imbalance failure of about 5-10 years with the older test conditions and greater than 50 years with the newer test conditions. Part of this change is also due to testing at 5 ppm ozone rather than 1 ppm ozone, which is a separate topic for future investigation.

The data presented here strongly argues for using a single average target test condition for comparing data between laboratories. Practically, some tolerance is necessary for sensor drift, calibration errors, and equipment feedback control systems. Based on these research findings, the recommended tolerances should be no more than +/-2C and +/-3% relative humidity for the sensors and calibration procedure. Moreover, constraints are recommended for the allowable deviation within a test run (due to the control system, etc.) such that the maximum deviation from the nominal target test condition does not exceed +/-4C and +/-10% relative humidity at any point during a test run, as sampled within every 5 minutes. As equipment capabilities continue to improve, the allowable tolerance range should be tightened accordingly.

Appendix

Table 8. Cyan Density Loss Data of all Systems and Environments during Ozone Fade Testing.

	Cyan Optical Density Loss								
System	23C/50%	19C/45%	27C/55%	23C/55%	23C/45%	27C/50%	19C/50%	19C/64%	27C/39%
1A	8.3%	6.8%	10.1%	8.7%	7.8%	8.9%	7.0%	8.8%	8.5%
1B	5.7%	5.0%	6.5%	5.7%	5.3%	6.1%	5.0%	5.6%	5.6%
2A	44.5%	35.7%	59.7%	51.5%	41.3%	48.3%	49.5%	69.0%	39.8%
2B	56.4%	48.1%	65.6%	60.7%	51.2%	58.8%	56.3%	76.4%	53.0%
3C	21.6%	14.7%	40.5%	30.0%	21.7%	26.6%	29.9%	56.7%	24.3%
4C	37.4%	27.6%	54.5%	45.1%	34.2%	41.7%	40.5%	64.7%	33.2%
5C	38.8%	28.4%	50.2%	43.5%	32.0%	42.2%	34.5%	53.2%	26.8%
6D	17.4%	14.5%	21.1%	18.4%	16.4%	19.9%	16.6%	24.0%	18.2%
7E	34.2%	27.6%	43.3%	39.2%	30.0%	36.7%	34.2%	56.2%	29.3%
7F	33.8%	30.0%	39.8%	37.0%	32.0%	37.5%	33.0%	44.8%	34.4%
8E	17.5%	13.9%	21.9%	19.7%	15.6%	19.3%	16.1%	29.4%	16.6%
8F	16.2%	12.9%	19.4%	16.5%	14.6%	17.3%	13.7%	21.6%	16.0%
9G	4.5%	3.5%	6.9%	4.9%	4.2%	5.5%	3.7%	6.0%	4.6%

Table 9. Magenta Density Loss Data of all Systems and Environments during Ozone Fade Testing.

	Magenta Optical Density Loss								
System	23C/50%	19C/45%	27C/55%	23C/55%	23C/45%	27C/50%	19C/50%	19C/64%	27C/39%
1A	2.5%	2.3%	3.2%	3.0%	2.4%	3.0%	2.4%	3.0%	2.6%
1B	2.6%	2.3%	3.2%	2.5%	2.3%	2.8%	2.3%	3.0%	2.5%
2A	52.3%	42.8%	68.8%	59.6%	49.9%	57.3%	52.9%	72.0%	50.3%
2B	66.1%	57.8%	75.6%	69.4%	62.3%	69.5%	64.0%	83.4%	69.1%
3C	34.9%	25.1%	55.5%	45.8%	34.5%	39.7%	38.2%	73.9%	35.3%
4C	50.0%	39.3%	67.7%	58.6%	46.8%	54.5%	48.6%	78.7%	44.9%
5C	77.6%	66.5%	85.6%	81.4%	70.3%	79.9%	71.0%	89.2%	58.6%
6D	13.3%	12.1%	15.9%	13.6%	13.3%	15.1%	11.7%	15.4%	14.9%
7E	31.3%	25.9%	39.4%	33.9%	29.9%	35.3%	28.8%	45.6%	32.4%
7F	39.9%	37.3%	45.6%	42.4%	40.4%	44.6%	38.1%	45.2%	45.0%
8E	8.0%	6.3%	9.5%	8.1%	7.4%	8.8%	6.8%	6.9%	8.8%
8F	12.8%	10.7%	14.0%	11.4%	12.1%	13.2%	10.7%	12.0%	15.2%
9G	4.3%	3.5%	6.1%	4.6%	4.4%	5.1%	3.9%	5.8%	5.3%

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.