Effect of Ozone on Rate of Paper Yellowing in Dark Storage Test

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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. To understand which variables to isolate for a given test method, it is necessary to investigate a broad range of conditions which may affect the test results. These variables may not have been controlled in the past, are difficult to control, or may not accurately reflect real world conditions. In a prior paper, it was shown that airflow can affect the rate of paper yellowing in a thermal stability test used to simulate dark storage conditions.

During that testing, additional sources of potential noise were identified that affected the test results. This paper focuses on additional thermal stability experiments that studied the influence of ozone exposure on the rate of paper yellowing under thermal test conditions. Moreover, due to the rapid yellowing of some microporous photo paper after exposure to ozone, it is also possible to compare the validity of an accelerated thermal test method in predicting results at ambient conditions. 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 potential impact of insufficiently controlled environmental ozone in a test method used to evaluate dark storage print image permanence [1]. Dark stability is estimated using the Arrhenius method by testing at a range of elevated temperatures and extrapolating to an assumed typical consumer storage condition. In prior testing it was found that the typical inkjet failure mode was not due to ink colorant failure, but paper yellowing [2]. That research used the existing failure criteria from ISO 18909 to determine the failure point according to changes in optical density. Alternatively, a delta E calculation may be considered to assess changes in paper white:

$$\Delta E = \sqrt{(L_1 * - L_2 *)^2 + (a_1 * - a_2 *)^2 + (b_1 * - b_2 *)^2} \qquad (1)$$

Using delta E compared to optical density for d_{min} (i.e. unprinted paper white) simplifies the analysis by reducing six calculations and failure criteria to only one, while at the same time providing consistent results with the first density calculation to reach failure.

Ongoing research on the method of thermal testing has found several factors that influence the results of the test. Research presented last year focused on the effect of airflow on the rate of paper yellowing as shown in Table 1.

Table 1. Failure Times from Four Media at Four Different Airflow Rates at a Single Test Temperature.

	Hours to Failure at 78C/50%			
Airflow	**Media A**	**Media C**	**Media K**	**Media M**
6±1m/s	636	1223	869	833
4±1m/s	669	1293	924	861
2±1m/s	738	1381	950	971
0 m/s	1295	2320	1143	1047

Other factors that may influence these results include light bleaching and contamination from other nearby test samples. These other factors will be explored in more detail in future work and for this study their contribution was minimized as much as possible.

The influence of ozone on paper yellowing was discovered when examining test samples that had been kept in storage for several months after an ozone stability test. A variety of commercially available media were observed to display significant yellowing; however, none had appeared yellow at the conclusion of the ozone stability test.

During the past year several separate experiments have been run to determine:

- which media are sensitive to ozone
- whether the concentration of ozone has an effect on paper yellowing
- whether the cumulative ozone exposure has an effect on paper yellowing
- and whether accelerated thermal tests accurately predict ambient performance.

Experiment

The following equipment was used in the dark stability 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
- ESPEC ESL-4CW environmental chamber
- Gretag Spectrolino/Spectroscan

Samples were conditioned with ozone in the MAST/Lunaire ozone chamber, and then measured prior to beginning the dark stability test. Since only the yellowing of the media was being studied, no color patches were printed on the test target as shown in Figure 1. Locating features were printed on the test target to ensure that the same paper white locations were measured after each test interval. A total of 28 measurements 1cm apart were taken on each sample, covering a space 6cm high by 3cm wide. The large number of measurements per sample averaged out any local point defects created during media manufacturing or handling [2].

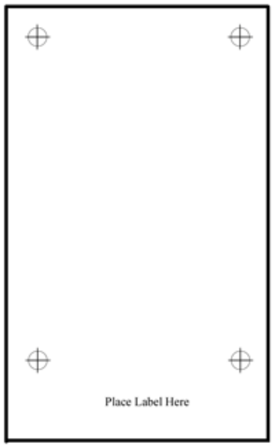

Figure 1. Test Target (Measurements of Paper White within Locating Features)

Several identical ESPEC environmental chambers were used to test the samples and each chamber was recalibrated with respect to the chilled mirror hygrometer at each test condition. The samples were all free hanging in accordance with ISO 18909.

Although some samples were deliberately exposed to ozone prior to the dark stability test, all the samples were in an ozone free environment during the dark stability tests.

Results and Discussion

The first series of tests determined which media were sensitive to ozone. In the airflow experiment both swellable and porous media were tested, but only porous media were found to be affected by airflow. The ozone sensitivity experiment extended the media selected to include plain media samples. This paper will use consistent sample identifications for porous media: A through Q, swellable media: R and S, and plain media samples: T and U.

Media were tested at a range of temperatures, but for conciseness only data from the 85C screening test will be reported. At that particular temperature there were three thermal tests conducted simultaneously within the same test chamber. One set of samples had not been pre-exposed to ozone while the other two sets had been pre-exposed to ozone and will be discussed later. Test measurements were taken at 20, 60, 200, 360, 520, 840, 1480, and 2100 hours. Table 2 shows a subset of results from the media not pre-exposed to ozone. The data was also used to calculate the time required for the paper yellowing to reach 10 delta E either by interpolating between the two measurements that bracketed the failure point or by linearly extrapolating from the last two measurements. Note that linear extrapolation usually under predicts actual time to failure because the paper yellowing is nonlinear, as can be seen in Figure 2. Over a third of the media tested were projected to take twice as long to fail as the actual test length. This is one of the drawbacks of thermal stability testing, as it took 3 months to run this one test. In addition, most thermal stability tests are run at lower temperatures, which take much longer to reach failure.

Table 2. Thermal Stability Test Data. Tested at 85C/50% (No Ozone Pre-exposure)

	Delta E at Time (Hours)				Failure
Media	**20**	**200**	**840**	**2100**	**Hours**
A	2.39	9.05	16.82	21.98	***253***
B	0.77	2.22	4.07	6.11	***4756***
C	1.54	5.46	11.86	17.85	***617***
D	0.79	2.18	4.02	6.11	***4727***
E	1.24	3.59	7.09	10.29	***1943***
F	2.56	5.42	9.52	14.17	***954***
G	2.51	4.70	7.05	10.26	***1966***
H	0.17	1.23	3.37	5.68	***4894***
I	0.17	1.60	3.99	6.51	***4202***
J	0.90	2.58	4.66	7.00	***3871***
K	1.35	5.61	14.02	24.37	***501***
L	0.77	2.86	6.99	12.58	***1450***
M	1.33	5.60	13.95	24.12	***502***
N	1.34	3.55	5.92	8.08	***3474***
O	1.99	5.42	9.47	13.88	***974***
P	0.69	2.05	3.81	5.93	***4841***
R	1.92	5.26	9.61	13.46	***943***
S	1.47	5.25	26.38	38.85	***377***
T	1.11	3.62	6.68	9.33	***2496***
U	1.20	2.71	4.40	6.38	***4647***

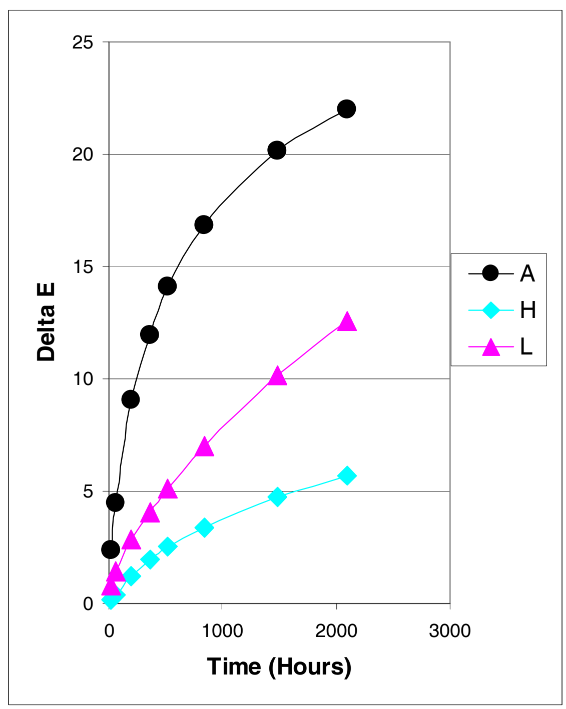

Figure 2. Delta E of Selected Media from Test at 85C/50% (No Ozone Pre-Exposure)

In the second of the parallel tests, samples were pre-exposed to 100 ppm-hours of ozone, at a concentration of 5 ppm ozone, prior to starting the thermal test. The data from this test is shown in Table 3. Just as in the earlier airflow experiment only the porous media were affected by exposure to ozone, while the swellable and plain media were not. While all the porous media yellowed faster with prior exposure to ozone, they did not do so at the same rate. For example, sample I yellowed about twice as fast when pre-exposed to 100 ppm-hours of ozone while sample K yellowed nearly 30 times as fast.

Table 3. Thermal Stability Test Data. Tested at 85C/50% (Ozone Pre-exposure at 5 ppm for 20 Hours: 100 ppm-Hours)

	Delta E at Time (Hours)				Failure
Media	**20**	**200**	**840**	**2100**	**Hours**
A	8.43	15.40	21.14	25.00	***43***
B	1.76	5.26	8.19	10.78	***1657***
C	9.75	16.59	22.36	26.66	***23***
D	1.96	5.25	7.99	10.63	***1751***
E	20.88	27.05	25.91	24.92	***10***
F	18.63	27.72	31.54	34.42	***11***
G	3.24	7.10	9.69	11.59	***1014***
H	1.81	5.24	8.00	9.99	***2106***
I	2.19	5.51	8.20	10.23	***1914***
J	7.62	13.17	16.35	18.60	***56***
K	11.81	18.63	25.72	32.72	***17***
L	13.21	19.15	23.96	27.75	***15***
M	13.35	19.97	26.86	33.84	***15***
N	2.01	5.24	7.80	9.98	***2117***
O	3.63	7.80	12.27	16.34	***450***
P	1.92	5.44	8.27	10.92	***1577***
R	2.04	5.47	9.86	13.67	***879***
S	1.57	5.59	26.97	39.21	***365***
T	1.21	3.91	7.21	9.79	***2224***
U	1.12	2.67	4.47	6.43	***4811***

The next question was whether the high pre-exposure ozone concentration was responsible for this accelerated paper yellowing in the thermal test. The samples in Table 3 had been conditioned at 5 ppm ozone for 20 hours, simulating about 1-2 years of ambient ozone exposure. A third group of samples were conditioned at 1 ppm ozone concentration for 100 hours for the same cumulative ozone exposure of 100 ppm-hours and run concurrently with the previous two tests.

Data from the lower ozone pre-exposure concentration is shown in Table 4. The results are very close to those from the pre-exposure at the higher ozone concentration. Media E, F and M showed the largest difference between the ozone exposure levels, but are far closer together than to the no ozone test condition reported in Table 2, as shown in Figure 3. Comparing delta E measurements and failure time calculations between Tables 3 and 4 also illustrates the concern that small changes in the delta E measurement can result in large differences in the failure time—due to the nonlinear rate of yellowing of these media. For media not affected by ozone the repeatability of the test results is confirmed with these series of experiments.

Table 4. Thermal Stability Test Data. Tested at 85C/50% (Ozone Pre-exposure at 1 ppm for 100 Hours: 100 ppm-Hours)

	Delta E at Time (Hours)				Failure
Media	**20**	**200**	**840**	**2100**	**Hours**
A	7.58	14.68	20.61	24.50	***56***
B	1.63	4.93	8.02	10.68	***1701***
C	8.43	15.39	21.17	25.91	***39***
D	1.82	4.99	7.78	10.46	***1841***
E	18.65	24.83	24.16	23.78	***11***
F	15.43	25.08	29.46	32.62	***13***
G	3.34	7.37	9.98	11.96	***850***
H	1.61	4.82	7.58	9.70	***2349***
I	1.97	5.14	7.83	9.94	***2153***
J	7.30	12.77	16.01	18.24	***64***
K	9.49	16.54	24.25	31.69	***27***
L	10.28	16.03	21.38	26.01	***19***
M	9.23	16.32	24.32	32.11	***31***
N	2.03	5.38	8.00	10.21	***1959***
O	3.42	7.62	12.02	16.17	***478***
P	1.67	4.89	7.82	10.49	***1825***
R	2.00	5.35	9.70	13.48	***920***
S	1.53	5.53	26.67	39.00	***370***
T	1.25	4.00	7.19	9.79	***2227***
U	1.19	2.71	4.54	6.57	***4407***

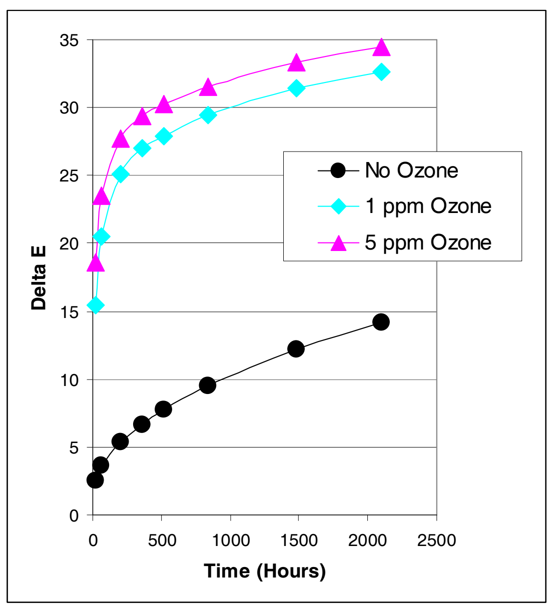

Figure 3. Delta E of Media F from Test at 85C/50% Comparing No Ozone Pre-Exposure with Ozone Pre-Exposure of 100 ppm-Hours

After determining that the pre-exposure ozone concentration had only a small effect on the rate of paper yellowing, the next step was to determine what kind of impact the cumulative ozone exposure had on paper yellowing.

Although tests were run at several temperatures, results at the 71C/50% test condition are illustrative of what happens to paper yellowing as a function of cumulative ozone exposure. For this series of experiments only porous media were used.

Table 5 shows a subset of the baseline data for 71C. Measurements were taken at 4, 10, 20, 40, 100, 160, 320, 640, and 1500 hours. Comparing with results for identical media in Table 2 demonstrates the increase in failure time when running at lower temperatures—about a 4 times average increase at 71C compared to 85C, ranging from twice as long to 8 times longer.

Table 5. Thermal Stability Test Data. Tested at 71C/50% (No Ozone Pre-exposure)

	Delta E at Time (Hours)				Failure
Media	4	20	100	1500	Hours
A	0.25	0.52	1.50	8.29	*2021*
B	0.39	0.43	0.78	2.58	*9461*
C	0.18	0.48	1.31	6.07	*3109*
D	0.37	0.37	0.66	2.35	*9990*
E	0.21	0.47	1.19	4.07	*5550*
F	0.64	1.07	2.12	5.21	*4568*
G	1.09	1.34	2.35	4.88	*5676*
H	0.14	0.27	0.15	2.09	*9222*
J	0.43	0.48	0.94	2.80	*8960*
K	0.29	0.39	1.00	6.56	*2523*
L	0.14	0.23	0.64	3.23	*6366*
Q	0.32	0.59	1.75	9.02	*1785*

Table 6 shows test results for the same media, pre-exposed to 100 ppm-hours of ozone, and Table 7 shows test results obtained for the same media pre-exposed to a cumulative ozone exposure of 2500 ppm-hours. There is a strong relationship between cumulative ozone exposure and the rate of paper yellowing; the relationship is also highly nonlinear for some media. For example, media E was highly sensitive to just a small amount of ozone and increasing the ozone exposure by 25 times resulted in only a small increase in the rate of yellowing.

The extraordinary yellowing of media pre-exposed to a cumulative ozone exposure of 2500 ppm-hours was unexpected and the first measurement at 2 hours was well past the failure criteria for several media. Because of the highly nonlinear yellowing this resulted in poor estimates of the failure time. Therefore another identical test was prepared and measurements were taken at 10 minutes, 20 minutes, 40 minutes, 1 hour, 2 hours, and 4 hours. Select test results are shown in Table 8. To accurately achieve such a short test time, the chamber was preheated to the desired set point and samples were placed in the chamber via a pass through and timed to within a few seconds. Comparing Tables 7 and 8 shows that some media yellowed about the same (e.g. Media B), but some did not (e.g. Media C and D). Moreover, failure times were over estimated by a factor of two for Media A and Q in Table 7 vs. Table 8.

Table 6. Thermal Stability Test Data. Tested at 71C/50% (100 ppm-Hours Ozone Pre-Exposure)

	Delta E at Time (Hours)				Failure
Media	4	20	100	1500	Hours
A	2.15	3.71	6.51	13.17	*533*
B	0.39	0.65	1.77	5.81	*3778*
C	1.73	4.47	9.24	15.36	*135*
D	0.44	0.79	1.94	5.53	*4258*
E	8.78	14.07	16.83	19.52	*6.2*
F	4.17	8.10	14.72	23.55	*35*
G	0.86	1.48	3.14	7.78	*2739*
H	0.32	0.48	1.82	5.46	*4078*
J	2.82	4.63	7.27	12.23	*446*
K	2.64	5.56	8.23	14.78	*359*
L	2.62	6.26	10.11	14.23	*97*
Q	2.48	4.46	7.31	14.00	*404*

Table 7. Thermal Stability Test Data. Tested at 71C/50% (2500 ppm-Hours Ozone Pre-Exposure)

	Delta E at Time (Hours)				Failure
Media	2	4	10	20	Hours
A	24.03	28.54	34.94	38.54	*0.8*
B	9.44	13.98	21.20	25.35	*2.2*
C	19.54	26.03	34.62	39.07	*1.0*
D	10.30	15.40	23.14	27.54	*1.9*
E	7.95	12.01	19.51	25.84	*3.0*
F	10.91	16.86	26.84	33.76	*1.8*
G	8.40	10.94	14.91	18.36	*3.3*
H	9.93	13.82	19.34	23.05	*2.0*
J	7.41	9.41	11.29	12.59	*5.9*
K	4.88	7.45	12.32	16.44	*7.1*
L	9.54	13.57	20.55	25.73	*2.2*
Q	26.33	30.85	37.08	40.50	*0.8*

The magnitude of paper yellowing between these tests at the common measurement points showed that some media had yellowed the same, while others had yellowed slightly more or less. A possible explanation for why media would yellow less in the follow up test is due to the bleaching effect of the office light (kept to a minimum) and the measurement itself. A reason why it might yellow more is if the reaction is continuing for a short time within the media after it is removed from the test environment (the same has been observed with ozone testing where samples fade slightly more with many short test cycles than fewer longer cycles to the same end exposure).

Table 8. Thermal Stability Test Data. Tested at 71C/50% (2500 ppm-Hours Ozone Pre-Exposure)

	Delta E at Time (Hours)				Failure
Media	0.17	0.33	1	2	Hours
A	5.99	8.84	15.71	22.63	***0.43***
B	0.97	1.83	4.92	9.45	***2.20***
C	2.78	4.49	10.14	17.39	***0.98***
D	0.91	1.66	4.62	9.14	***2.30***
E	1.06	1.79	3.93	6.76	***3.52***
F	1.29	2.15	5.06	9.42	***2.18***
G	2.28	3.41	6.65	9.82	***2.14***
H	2.11	3.27	6.33	10.22	***1.94***
J	2.00	3.27	6.02	8.44	***3.31***
K	1.01	1.49	2.95	4.83	***5.80***
L	1.44	2.37	5.11	8.42	***2.73***
Q	7.07	10.15	17.82	24.83	***0.33***

Table 9. Thermal Stability Test Prediction of Ambient 23C/50% Performance (2500 ppm-Hours Ozone Pre-Exposure)

	Time (Hours) to 5 Delta E	
Media	Predicted	Actual
A	340	390
B	580	> 20000
C	300	1250
D	610	> 6000
E	960	> 4700
F	910	> 2500
G	820	> 2300
H	770	> 3900
J	620	830
K	2000	> 14000
L	1100	> 4800
Q	230	260

With the observation that porous media exposed to ozone yellow quickly in accelerated thermal testing, it presented the opportunity to check the accuracy of the thermal test method. Previously, testing at lower temperatures would take years to reach completion, and testing at ambient conditions would take decades or centuries. However, by exposing some media to ozone the length of the test is shortened by orders of magnitude.

A test with media pre-exposed to 100 ppm-hours and 500 ppm-hours of ozone was started at ambient dark conditions (23C, 50%RH) late in 2007 and at the time this paper was written had run for over 4600 hours. The results are both startling and inconclusive and time does not allow further discussion here, but one important observation is that several porous media are showing reversal of the yellowing process. This has already been shown with Media E in Tables 3 and 4, so it is not an isolated situation and warrants further investigation.

A second ambient test was started with only porous media pre-exposed to 2500 ppm-hours of ozone. At the time this paper was written it had run for over 1800 hours. Three other groups of samples pre-exposed to the same amount of ozone were tested at 71C, 57C, and 43C. In accordance with ISO 18909, the Arrhenius method was used to predict the ambient performance of these media and then compared to the actual ambient measurements. Table 9 shows the predicted time (from the accelerated tests) to reach 5 delta E compared to the actual time (from the ambient conditions test). Since the ambient test had only run to 1800 hours, higher values are extrapolations and are likely under estimations.

The common theme is that the Arrhenius method is under predicting the actual failure time for all media. And although some predictions appear close, the situation changes when using 10 delta E. For example, Media Q was predicted to reach 10 delta E in 500 hours while it took 1450 hours in the actual test. Media A was predicted to get there in 700 hours, and in the actual test the extrapolated prediction is over 3000 hours. And Media J was predicted to get there in 1880 hours, while the actual test is projecting it will take over 4000 hours. Figure 4 demonstrates how the Arrhenius extrapolation begins to deviate from the actual test measurements for larger changes in delta E.

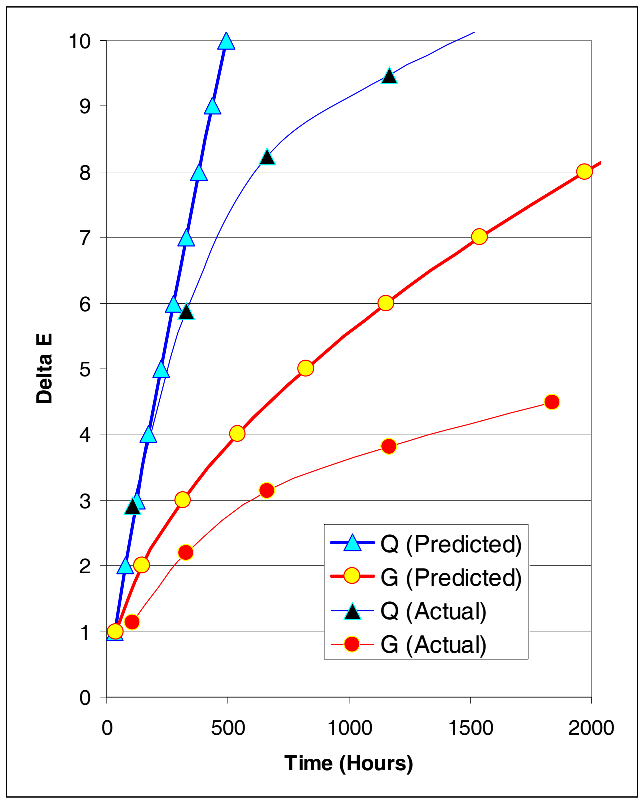

Figure 4. Predicted and Actual Delta E Performance of Media Q and G at Ambient Test Condition of 23C/50%.

Before discussing potential reasons for this outcome, it is important to note that the range of accelerated test temperature data on the Arrhenius plot is extremely linear. The discontinuity is therefore occurring between the accelerated tests, as a group, and the ambient test. It has previously been stated that light bleaching can affect the yellowing of the media. Each time a sample is measured, it is exposed to a short burst of high intensity light.

Samples run at ambient were measured more frequently at equivalent delta E compared to an accelerated test. However, a more plausible explanation is due to a difference in airflow, since the ambient test was run with nearly no airflow (free hanging and passive ventilation) while the accelerated tests were run in environmental chambers with an average airflow closer to 1 m/s. Higher airflow results in faster paper yellowing for the porous media tested—which would be consistent with this data.

Conclusion

Since the Arrhenius test is run with different samples at a range of temperatures, if some of those samples are contaminated with ozone prior to testing it can result in large errors in the life predictions. Figure 5 shows an Arrhenius plot with realistic test data for a single media where some of the samples tested at higher temperatures are contaminated with ozone while the others are not. Even though the test data has good linearity for both sets of data, it is predicting 850 years at 23C for the uncontaminated samples and over 8000 years for the contaminated samples. The reason shorter life is not predicted is because not all the samples used in the Arrhenius plot were equally contaminated. The same problem occurs when simultaneously testing in different chambers with different airflows at a range of temperatures to fulfill the Arrhenius method requirements [2].

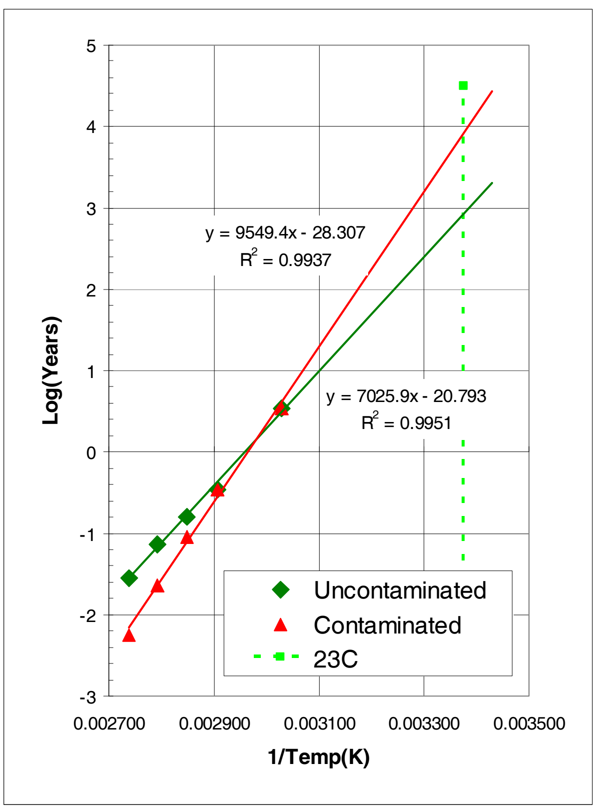

Figure 5. Scenario for Poor Life Prediction Based on Arrhenius Method with Some Media at Higher Temperatures Contaminated by Ozone Pre-Exposure.

A large selection of commercially available porous media was found to yellow faster when exposed to ozone. This was not the case with the swellable or plain media tested. The concentration of ozone was found to have a minor impact on the rate of paper yellowing; while increasing the cumulative ozone exposure resulted in faster paper yellowing. However, the relationship is highly nonlinear and some media exhibited a threshold behavior, reacting strongly to a relatively low cumulative ozone exposure.

It can be difficult to get consistent test results in a dark stability test. The data presented in this paper shows that exposure of unprinted media to air containing environmental ozone prior to testing can influence dark storage test results. Based on these findings, it is recommended that media be kept in the package until ready for printing. Printed media should also be dried in an ozone free environment prior to testing and during measurements.

The accuracy of the Arrhenius method was also explored. Based on ongoing ambient testing, it was found that the accelerated tests uniformly under predicted the actual ambient failure times. Although this error is conservative, it raises a concern. This is because the Arrhenius method relies on tests at several temperatures. If a test at a higher temperature is influenced by noise factors which cause samples to fail faster (i.e. airflow, ozone), while tests at lower temperatures are not influenced to the same extent by those noise factors, then the Arrhenius method will over predict actual sample life at ambient conditions.

It was also shown that the failure times for individual tests were dependent on the frequency of the measurements around the failure criteria because paper yellowing is often nonlinear. Therefore, it is recommended that measurements bracket the chosen failure criteria to within 10%.

Finally, based on this data it may be tempting to dismiss paper yellowing as too difficult to assess in a standardized test method. However, simply eliminating paper yellowing from a set of failure criteria doesn't resolve the problem, since it will also confound measurements of color patches (e.g. light yellow patch density is affected by paper yellowing). Future work will continue to focus on improving the consistency and relevance of the dark stability test.

References

[1] ISO 18909 Photography – Processed photographic colour films and paper prints – Methods for measuring image stability.

[2] M. Comstock, A. McCarthy, P. Sacoto, R. Silveston-Keith, "Effect of Airflow on Rate of Paper Yellowing in Dark Storage Test Conditions", Final Program and Proceedings of IS&T's NIP23: International Conference on Digital Printing Technologies, Anchorage, Alaska, pp. 716-720 (2007).

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.