Validity of Dark Storage Test Method

Matthew Comstock, Ann McCarthy; Lexmark International, Inc.; Lexington, Kentucky, USA

Abstract

The dark storage test relies on elevated temperatures to accelerate aging of print materials that are kept in photo albums, file cabinets, shoe boxes and other enclosed containers. However, the widely used free hanging test method in dark storage testing of print images does not simulate the actual consumer storage condition. Few studies have been performed to check the validity of the accelerated thermal test for print images because the accelerated tests themselves can take months or years to complete. Earlier research into the sources of noise in the dark storage test found that porous photo papers exposed to ozone prior to starting the accelerated thermal test would fail much faster. By deliberately pre-conditioning porous photo papers with ozone it is possible to accelerate these media thermal tests by orders of magnitude. This makes it possible to finally compare ambient real world dark storage test results to testing at elevated temperatures. This paper will describe those observations, which include some unexpected but repeatable results.

Introduction

The Arrhenius method for estimating dark storage of print samples has been the most enduring of the image permanence tests. The test method has not been significantly altered for decades and allows for direct predictions of ambient performance. However, it has been the authors' experience in using the free hanging test method for dark stability that the data is inconsistent, and this is especially true with porous photo paper tests. Some of the factors that influence the test results relate to handling: whether the media has been exposed to airborne contaminants, and whether the media is exposed to ambient light during measurement or testing. Other factors that influence the test results are whether tight control of temperature and humidity in the test chamber is maintained, whether there is airflow across the samples, and whether other test samples are present in the test chamber [1].

The dark storage test, also referred to as dark stability or thermal stability, often provides life estimates of hundreds or thousands of years. There are bold claims made on photo media packaging based on these test results. But how reliable are the test results? The sheer length of time required for thermal stability testing seems to preclude the possibility of verifying these results. Fortunately, it was discovered that many porous photo papers will degrade much more quickly after being exposed to ozone [2]. Testing has demonstrated that one can start with two identical sets of media, leave one set sealed and protected while the other is pre-conditioned with a controlled ozone dose, and then compare both sets again and find that they are still identical visually. However, once removed from the ozone, some media begin to yellow much more quickly [2]. This altered behavior allows elevated thermal stability tests to be completed in hours instead of months. Moreover, verification of results at ambient temperatures is now possible in months rather than in decades or centuries.

Experiment

The equipment used in this investigation is identical to the referenced studies. Sample test targets and preparation also remain the same. One key difference is the magnitude of the initial ozone pre-exposure dose, which was 500 hours at 5 PPM, or 2500 PPM-hours of ozone. Such a large dose was probably not necessary, but ensured an adequate response of the media in an ambient test requiring 6 months to complete.

Prior to this particular experiment, the authors had attempted several ambient thermal stability tests. Each of these tests ran between 8 to 12 months and exhibited unusual behavior. To eliminate any outside influences for this test, great care was taken in the sample handling and measurement. For example, samples were transported and measured in the dark (office lights were turned off and flashlights used). Moreover, the ambient air testing was conducted in a specially designed cabinet located in an environmentally controlled lab at 23C/50% RH with filtered air. This cabinet was designed to keep the samples dark during testing while also providing slow air exchanges with the surrounding filtered lab air.

The elevated temperature tests were run at 37C/50% RH, 50C/50% RH, and 64C/50% RH. The 37C test was measured at 2, 10, 40, 100, 200, and 500 hours. The 50C test was measured at 2, 4, 8, 20, 40, and 100 hours. The 64C test was measured at 0.5, 1, 2, 4, 8, and 20 hours. For the first few measurements at each temperature, the samples were introduced into the chamber after it had reached the test temperature. This is because the typical 15-minute temperature ramp up would have introduced a large error into the test.

The study evaluated both the standard free hanging test method as well as the recently proposed sandwich test method [1]. The sandwich method used in this study was the originally proposed method using the same media as the test sample. Another series of experiments have been started using the newer sandwich method with polyester film, but data is not yet available for comparison.

Results and Discussion

Because the ambient test ran for over half a year, two Gretag Spectrolino Spectroscans were used to take measurements as a precaution in case one of the instruments failed. Having two sets of measurements from two separate spectrometers also permitted a direct comparison between them. It was found that for most of the media tested, the deviation between the instruments was less than 0.1 delta E, with a few media up to 0.2 delta E. This corresponded to about 1-2% deviation. There were 4 media which showed consistently larger deviations between devices right from the start of the test. Since this was isolated to only these media, the problem was determined to be related to the inherent measurement capabilities of the spectrometer rather than due to instrument drift.

A large number of commercially available media were evaluated in this study and are identified by the letters A through Y. The majority of the media tested are porous photo papers, but samples of swellable, matte coated, and plain paper were included as well. Figure 1 shows data collected from two different porous photo papers on both spectrometers (identified as '2' and '4') in the free hanging ambient temperature test. As can be seen, both devices measured nearly the same delta E values when measuring the same media. Another observation from this plot is the erratic change in paper yellowing. This erratic behavior is similar to what was observed in earlier ambient thermal tests: a reversal in media yellowing. It was originally believed to be from light bleaching, but this test had taken extra precautions to eliminate incidental light exposure. That both spectrometers are showing it also rules out the possibility of random instrument variation or improper calibration.

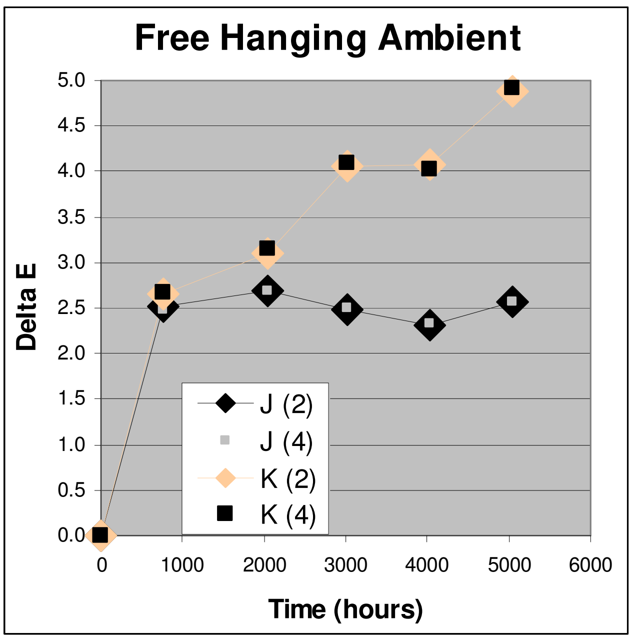

Figure 1. Measurements of media J and K using Free Hanging Method in Ambient (23C/50%) test condition. Measurements are shown of the exact same samples using two different measurement devices (2) and (4).

Table 1 shows all the measurement data for the ambient thermal test using the free hanging method. The 3 media with the least amount of yellowing are swellable, matte, and plain papers: D, E, and Y respectively. The media with temporary reversals in yellowing are: A, B, C, F, G, H, I, J, K, L, M, O, P, Q, R, S, T, U, W, and X. Not shown is data from a simultaneous test at ambient temperature using the sandwich method. The sandwiched media samples showing yellowing reversal are: E, F, G, and J. The sandwich method resulted in less severe reversals; moreover, an ongoing test using the newly proposed sandwich method with polyester film is showing no yellowing reversals in the ambient thermal test. These comparisons suggest that the cause of the reversals is related to the air exposure during the dark stability test.

Table 1. Measurement values during ambient test (23C/50%) of media using Free Hanging Method.

	Delta E at Indicated Time (Hours)						
Media	**360**	**760**	**1370**	**2040**	**3020**	**4030**	**5040**
A	6.28	9.48	10.98	11.73	12.72	12.55	13.99
B	3.38	5.60	6.66	7.75	8.67	8.60	9.26
C	2.39	4.65	5.56	6.57	7.19	6.69	8.12
D	0.07	0.12	0.15	0.18	0.23	0.25	0.27
E	0.12	0.33	0.39	0.48	0.58	0.65	0.75
F	2.28	4.53	5.33	5.81	5.88	5.25	5.95
G	0.59	1.05	1.07	1.16	1.12	1.07	1.20
H	0.90	1.75	1.99	2.22	2.13	2.00	2.28
I	1.98	3.47	4.13	4.47	4.27	4.17	4.53
J	1.29	2.49	2.59	2.69	2.50	2.33	2.57
K	1.51	2.66	2.93	3.15	4.10	4.03	4.91
L	1.36	2.68	3.54	4.08	5.51	5.61	6.99
M	1.33	2.60	3.10	3.51	4.39	4.28	5.16
N	1.85	3.55	4.73	5.71	7.32	7.44	8.93
O	2.32	3.90	4.42	4.67	5.50	5.48	6.79
P	3.39	5.43	6.81	7.72	8.62	8.52	8.89
Q	2.01	3.55	4.28	4.62	5.19	4.74	5.67
R	3.32	5.44	6.75	7.68	8.63	8.47	9.14
S	7.48	12.17	15.34	16.62	18.16	17.65	19.33
T	5.40	8.97	11.10	12.26	12.90	12.07	13.58
U	0.79	1.42	1.60	1.68	1.77	1.66	1.87
V	1.25	1.96	2.06	2.24	2.36	2.37	2.73
W	4.37	7.35	9.24	9.71	10.33	9.99	10.95
X	5.77	9.59	11.97	13.06	13.61	13.10	14.11
Y	0.14	0.27	0.39	0.48	0.59	0.66	0.76

One basis of the standardized testing is that the yellowing behavior of any given media should be consistent within the range of temperatures tested in the dark stability test. To see whether this was the case, the measurement data from all the media at each test temperature were compared. It was found that while many of the elevated temperature tests using the free hanging method were consistent with each other, there was a discontinuity in behavior when comparing to the ambient test data. Figure 2 shows an example of this by plotting the free hanging measurement data for media W. In order to make visual comparison between the tests easier, the time scale was normalized for each temperature data set according to when the media passed the failure threshold of 10 delta E in that data set. As can be seen, the plot shows excellent agreement between the 3 accelerated tests at 37C, 50C, and 64C; however, the ambient test at 23C showed far more yellowing at the beginning of the experiment. This data may also be viewed in an Arrhenius plot, as depicted in Figure 3. In that figure, each data point represents the time to failure at that temperature. The ambient temperature data point is at the upper right corner of the plot. The dashed line through the elevated temperature data is the best fit for the accelerated tests. If that dashed line is extrapolated to the 23C temperature line it intersects at a point far below the actual failure point of the ambient temperature test.

Figure 4 shows measurements from media W using the sandwich test method. This time the behavior of the ambient test is closely aligned with the elevated temperature tests. This is also evident in the Arrhenius plot shown in Figure 5.

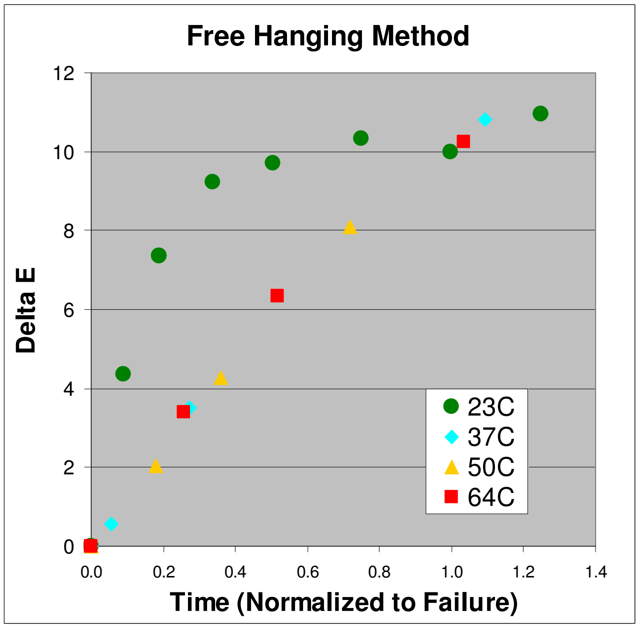

Figure 2. Measurements of media W using Free Hanging Method for accelerated tests at 64C, 50C, and 37C compared with ambient test at 23C with time scale normalized to a 10 delta E failure threshold.

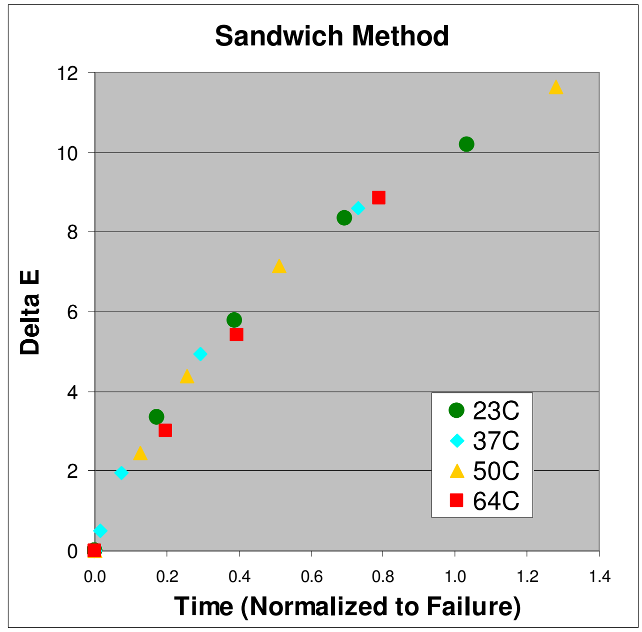

Figure 4. Measurements of media W using Sandwich Method for accelerated tests at 64C, 50C, and 37C compared with ambient test at 23C with time scale normalized to a 10 delta E failure threshold.

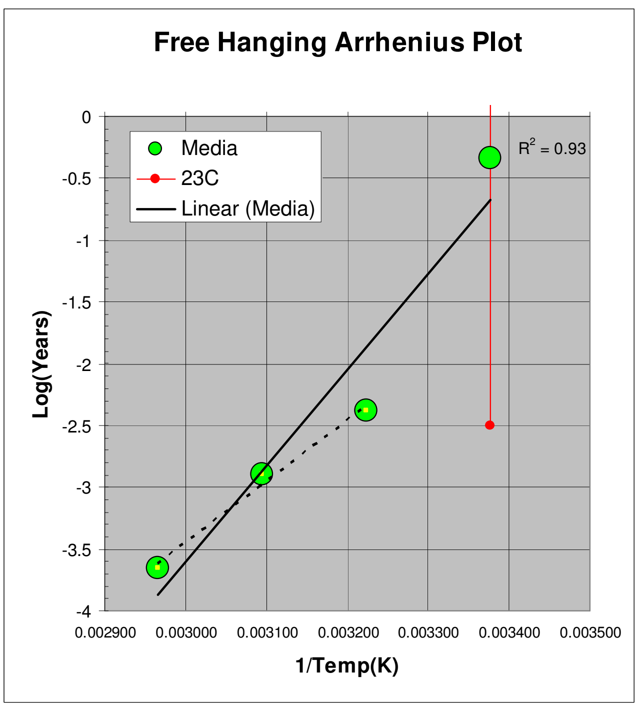

Figure 3. Arrhenius plot of media W using Free Hanging Method for accelerated tests at 64C, 50C, and 37C compared with ambient test at 23C.

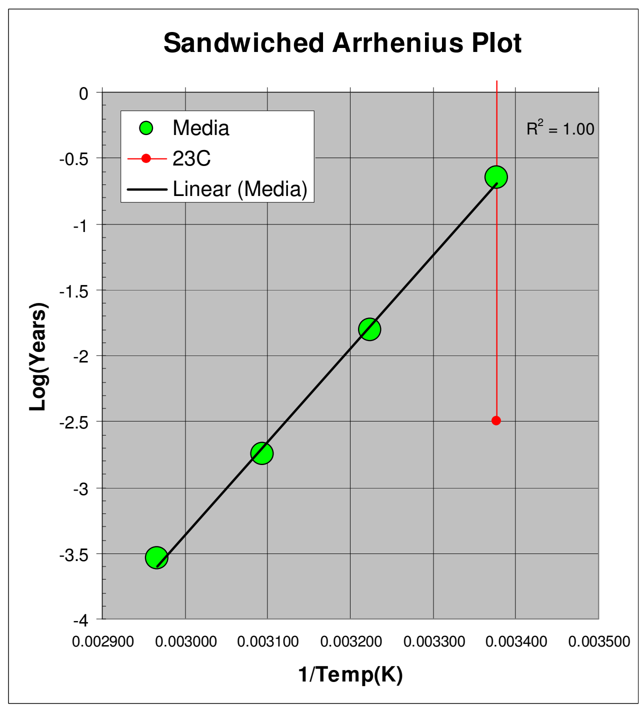

Figure 5. Arrhenius plot of media W using Sandwich Method for accelerated tests at 64C, 50C, and 37C compared with ambient test at 23C.

Referring back to Figure 3, according to the Arrhenius method, the point at which the extrapolated dashed line crosses the 23C temperature line is the predicted life estimate at ambient based on the accelerated tests. For media W this value is 228 hours using the free hanging method. The actual ambient test took just over 4000 hours to reach failure, so the ratio between predicted and actual failure time was 0.06. In contrast, the accelerated tests using sandwich method predicted that media W would fail in 1364 hours. The actual failure time of media W in the sandwiched ambient test was just under 2000 hours, so the ratio between predicted and actual failure times is 0.69. A ratio of 1 represents perfect agreement. While it is good to be conservative in life predictions, there is no value in having a life prediction that is an order of magnitude lower than the actual life.

By using the ratio between predicted and actual failure times, all the media results can be condensed into a single table rather than comparing dozens of figures. Table 2 shows these results for all the media. Note that because some media yellow much more slowly than others, for those media the failure threshold was adjusted down to either 5 or 2 delta E in order to minimize any errors associated with extrapolating to the failure threshold.

Among all the media tested in the free hanging method, the plain paper (media Y) had the best agreement between predicted and actual life with a ratio of 0.62. The ratio was not much better for this media using the sandwich method with the same media, but this was expected since separate testing had already confirmed that plain paper was ineffective as a sandwiching material.

The average of all the failure time ratios using the free hanging method was 0.20, and 0.49 using the sandwich method (excluding media T). Thus the sandwich method is more effective in producing accurate prediction results from the Arrhenius method than the free hanging method. However, the accuracy of the test method is still disappointing.

Conclusion

By exploiting the otherwise undesirable property of many porous photo papers to yellow more quickly after being exposed to ozone, it was possible to check the validity of dark storage testing using elevated test temperatures and the Arrhenius method to predict ambient image stability. The results showed that the free hanging test method underestimated the actual failure time by an average factor of 5, while the sandwich test method underestimated dark storage permanence by an average factor of 2.

While it is reassuring that the dark storage life predictions from the accelerated thermal test conditions underestimate the actual life, the value of the test method decreases with that corresponding loss of accuracy. Additional testing of the sandwich method using polyester film as a sandwiching material is showing further improvements, especially in a new ambient test currently in progress. Future updates will be documented as data is collected.

Table 2. Hours to failure for free hanging and sandwich test methods at 23C/50% RH.

	Failure Threshold	Hours to Failure (actual test to 5000 hours)					
		Free Hanging (23C)			Sandwiched (23C)		
Media	Delta E	Predicted	Actual	Ratio	Predicted	Actual	Ratio
A	10	192	974	0.20	347	1026	0.34
B	5	170	656	0.26	269	735	0.37
C	5	227	999	0.23	468	955	0.49
D	2	10348	99020	0.10	15550	21923	0.71
E	2	1345	16857	0.08	1097	9607	0.11
F	5	310	1118	0.28	363	707	0.51
G	2	264	11244	0.02	409	1644	0.25
H	2	261	1399	0.19	640	1254	0.51
I	2	126	367	0.34	248	378	0.66
J	2	150	601	0.25	154	330	0.47
K	2	142	532	0.27	363	638	0.57
L	5	310	2672	0.12	377	1344	0.28
M	5	427	4857	0.09	810	1514	0.53
N	5	256	1552	0.17	289	953	0.30
O	5	233	2428	0.10	465	1104	0.42
P	5	226	680	0.33	252	726	0.35
Q	5	208	4312	0.05	720	1498	0.48
R	5	186	681	0.27	281	756	0.37
S	10	185	578	0.32	700	1004	0.70
T	10	467	1056	0.44	2194	1273	1.72
U	2	290	5703	0.05	786	829	0.95
V	2	196	990	0.20	213	557	0.38
W	10	228	4039	0.06	1364	1971	0.69
X	10	198	868	0.23	860	1242	0.69
Y	2	11606	18820	0.62	11880	17472	0.68
			Average	0.20		Average	0.49

References

[1] M. Comstock, A. McCarthy, "Improved Dark Storage Test Method", Final Program and Proceedings of IS&T's NIP25: International Conference on Digital Printing Technologies, Louisville, Kentucky, pp.114-117 (2009).

[2] M. Comstock, A. McCarthy, "Effect of Ozone on Rate of Paper Yellowing in Dark Storage Test", Final Program and Proceedings of IS&T's NIP24: International Conference on Digital Printing Technologies, Pittsburgh, Pennsylvania, pp.231-236 (2008).

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.