Improved Dark Storage Test Method

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

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, may be 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 continues that investigation by showing that the presence of other test samples in the thermal test can influence the results; that is, samples can cross contaminate each other in the thermal test. This paper also details the development of a new test method which minimized the effect of cross contamination of samples within the thermal test. Moreover, the new test method also reduces variation in test results caused by varying airflow, either by position within the test chamber or due to testing in chambers of differing design. This research is part of ongoing work contributing to the development of standardized test methods for image permanence.

Introduction

Prior investigation of the thermal test intended to simulate dark storage conditions revealed that a number of unknown sources of noise were contributing to significant variation in the test result [1]. In particular, free hanging samples frequently were found to yellow more than expected based on the predictions from the forced airflow test samples.

In the previous testing many samples were evaluated together in the chamber due to lack of time to run samples individually and sequentially. During the airflow testing there were times when the free hanging sample set was by itself in the chamber and at other times the free hanging sample set was present along with the forced airflow apparatus. Based on observation, it was theorized that samples were being influenced by the other samples present in the test chamber.

Several experiments were designed to investigate whether the presence of other samples within a test chamber at the same time could influence the results of the test.

Experiment

The following equipment was used in the dark stability testing:

- Teledyne 400E UV Absorption O3 Analyzer
- Kahn Optidew Bench chilled mirror hygrometer
- ESPEC ESL-4CW environmental chamber
- ESPEC LHU-112 environmental chamber
- Gretag Spectrolino/Spectroscan

To investigate the possibility of samples influencing each other several media were selected for testing, designated by the letters A through E, representing a variety of manufacturers. These media, hereafter referred to as the sample set, were prepared and analyzed following the procedure described in earlier research [2]. In summary this involved:

- Using unprinted samples.
- Measuring each sample 28 times (3x6cm grid).
- Using delta E analysis with 10 delta E failure threshold.

These studies also included three identical samples per test condition to better assess repeatability.

Based on prior work in which airflow was found to influence the results of thermal stability testing, an alternative method of testing was devised that combined some attributes of the existing free hanging and sealed bag methods.

The proposed method involves taking the test sample of interest and placing it between two other identical samples and then holding the three samples together along their edges. Brackets from our Atlas Ci4000 Xenon test unit were used in this study, as they provided a firm grip along the outside edge of the samples, preventing airflow between the layered samples. The exterior samples (hereafter referred to as "dummy" samples) were not measured during the test; their sole role was to provide a physical buffer between the test sample and the chamber test environment. This physical buffer mimics the dark storage condition the thermal test is meant to simulate: images kept in an album, scrap book, or 'shoebox'. In these storage conditions, the images may be in contact with or stacked with others of the same kind and there is little to no airflow. This proposed method will be referred to as the "sandwich" method, because the test sample is sandwiched between two dummy samples. The Atlas brackets conveniently had hooks, which were used to free hang the sandwiched sample groups from the wire shelving within the environmental test chamber.

This paper will describe a series of experiments that investigated:

- whether free hanging samples of the chosen sample set could be influenced by additional samples in the test chamber;
- whether the sandwich method mitigated that influence;
- whether the sandwich method reduced variation observed in free hanging tests between different styles of environmental test chambers.

Results and Discussion

The first investigation involved testing the entire sample set together along with additional samples that were thought to potentially influence their behavior in the thermal test. Based on previous testing it was known that exposing porous photo media to ozone would accelerate the rate of media yellowing. Therefore, several media samples that had been pre-exposed to ozone were introduced into the same chamber along with the sample set. A test condition of 85C/50%RH was chosen for all tests and the sample set was measured at 160 hour intervals. Both free hanging and sandwiched samples were present during this test.

Once the first test was completed, a second test with a fresh set of free hanging and sandwich test samples was started in the same chamber with the same operating conditions. This time, no additional samples were present in the chamber.

The results of the free hanging samples in these two tests are shown in Table 1. Four media are listed along with their delta E measurement data throughout the test. The presented measurement values of all tests are each an average of 84 measurements (28 measurements per sample with 3 sample replicates). Using a failure threshold of 10 delta E, a time to failure was calculated using either linear interpolation or extrapolation. In the case of media D, the extrapolation is shown, but is uncertain. The deviation between the two test cases where either additional samples were present ("contaminated") or not present was calculated based on the failure time and from the average delta E measurement.

The test chamber has a volume of one cubic meter. Placing four sheets of additional media in the chamber resulted in nearly 25% faster yellowing of Media A and B. On the other hand, free hanging samples of Media C showed little impact from the additional test samples except during the first two test cycles.

Table 2 shows results from these same tests but now only comparing the sandwich method samples. The measurement deviation is mostly within the noise of the test method and makes a strong case that the exterior dummy samples were protecting the interior test samples from whatever contaminating influence was created by the additional samples in the chamber.

Comparing the results of the two methods as shown in Tables 1 and 2 shows that Media A, B, and C yellowed more slowly using the sandwich method while Media D yellowed much faster than free hanging samples. It was expected that without airflow the media would yellow more slowly, so the result from Media D was unexpected. This behavior warrants further investigation given that the sandwich test method better approximates typical consumer storage.

To further investigate whether samples could influence each other in the thermal test, a third experiment was designed utilizing only the sandwich method. The test samples were sandwiched with the same media, with the distinction that in one set the dummy samples were new ("fresh" from package) while in the other set the dummy samples had been pre-exposed to ozone. This is an extreme version of the earlier contamination test, since surface area of the test sample was now matched to the potential contaminating source. Table 3 shows results from this extreme contaminating experiment. Results were similar to the previous free hanging contamination study, except that in this case Media C was also shown to be influenced.

A fourth series of experiments was conducted to thoroughly investigate whether some of these media were affecting themselves as well as to determine whether the sandwich method could reduce variation observed between different test chambers. This study included two identical chambers (ESPEC ESL-4CW), and a third much older and smaller chamber (ESPEC LHU-112).

The focus of this last study was on Media C and D. Both were tested using the free hanging method and sandwich method. In addition to sandwiching each media with the same dummy samples, they were also sandwiched with the other media, and with a third media (Media E).

The conditions in each test chamber were matched using a chilled mirror hygrometer. To illustrate how important it was to match conditions, a small error was discovered in the first test within the smaller LHU-112 chamber. The chilled mirror hygrometer sensor cables were too large to pass through the side port so they were passed through the door. Although the door could be closed there was a gap between the glass inner door and the sealing gasket. This gap was filled with insulating material during the calibration process. However, when the initial sample delta E measurements were taken the data was suspicious so another temperature measurement was taken. Results indicated that some air may have been leaking through the front door, so the second measurement was only taken with the temperature sensor, which was small enough that it could be passed through the side port. It was found that the temperature was 86C rather than the targeted 85C. Apparently enough air was getting into the chamber during the initial calibration to create a 1C temperature gradient between the center of the chamber where the calibrating sensor was located and the chamber sensor in the upper back corner of the chamber.

The effect of that 1C temperature difference can be seen in Table 4. Media C free hanging samples yellowed over 25% more while Media D free hanging samples yellowed 7% more. A majority of the sandwiched samples yellowed between 10-15% more. As described in earlier work, small deviations such as this can result in larger variances in the predicted failure times, which can be magnified even further when incorporated into the Arrhenius method.

Measurements in all three chambers at identical test conditions of 85C/50% were collected every 160 hours and run to 800 hours total. A representative delta E measurement from 640 hours into the test is shown in Table 5. An average percent deviation of all five measurement intervals was calculated between the two identical Espec ESL-4CW chambers and then again between them and the smaller Espec LHU-112 chamber. As expected there was good agreement between the two identical test chambers for both free hanging and sandwich test methods with about 1-3% deviation (within the noise); however, the LHU-112 caused greater yellowing of the free hanging samples compared to the ESL-4CW. Media C yellowed 34% more, while Media D yellowed 9% more. Fortunately the sandwich method samples of Media C only yellowed 2% more—a tenfold improvement compared to the free hanging samples. And the sandwich method samples of Media D only yellowed 3% more—a threefold improvement.

One explanation as to why free hanging samples yellowed more in the LHU-112 is due to the different airflow pattern because samples are much closer to the fan. Moreover, it is also plausible that the increased sample surface area with respect to the chamber volume caused increased cross contamination of samples.

Table 1. Thermal Stability Test Data. Results of Two Tests With Standard Free Hanging Test Condition at 85C/50% Comparing Results When Other Samples Outside Sample Set Are Present ("Contaminated") or Not Present ("—").

	Free Hanging	Delta E at X Hours (85C/50%)				Failure	Failure	Measurement
Media	**Condition**	**160**	**320**	**480**	**640**	**(Hours)**	**% Dev**	**% Deviation**
A	--	4.82	7.54	9.80	11.50	**499**	**25%**	**22%**
A	Contaminated	6.53	9.39	11.22	13.21	**373**		
B	--	5.73	8.66	10.99	12.81	**412**	**31%**	**22%**
B	Contaminated	7.35	10.76	12.88	15.13	**284**		
C	--	3.55	5.63	7.41	8.96	**778**	**2%**	**6%**
C	Contaminated	4.04	5.96	7.41	8.73	**793**		
D	--	3.54	4.42	4.96	5.60	**2312**	**7%**	**6%**
D	Contaminated	3.73	4.67	5.35	5.80	**2147**		

Table 2. Thermal Stability Test Data. Results of Two Tests With Proposed Sandwich Test Method at 85C/50% Comparing Results When Other Samples Outside Sample Set Are Present ("Contaminated") or Not Present ("—").

	Sandwich	Delta E at X Hours (85C/50%)				Failure	Failure	Measurement
Media	**Condition**	**160**	**320**	**480**	**640**	**(Hours)**	**% Dev**	**% Deviation**
A	--	4.31	6.99	9.24	11.17	**543**	**0%**	**1%**
A	Contaminated	4.37	7.09	9.22	11.15	**545**		
B	--	4.56	7.22	9.38	11.24	**534**	**5%**	**3%**
B	Contaminated	4.70	7.53	9.67	11.57	**508**		
C	--	3.27	5.18	6.73	8.05	**917**	**6%**	**3%**
C	Contaminated	3.39	5.37	6.89	8.20	**859**		
D	--	5.07	7.62	9.89	12.03	**488**	**1%**	**1%**
D	Contaminated	4.99	7.67	9.95	12.10	**484**		

Table 3. Thermal Stability Test Data. Results With Proposed Sandwich Test Method at 85C/50%. Samples Sandwiched With Either Fresh New Same Samples or Ozone Pre-Conditioned Same Samples.

		Delta E at X Hours (85C/50%)				Failure	Failure	Measurement
Media	**Sandwich**	**160**	**320**	**480**	**640**	**(Hours)**	**% Dev**	**% Deviation**
A	New	4.37	7.09	9.22	11.15	**545**	**20%**	**17%**
A	"Conditioned"	5.27	8.26	10.66	12.79	**436**		
B	New	4.70	7.53	9.67	11.57	**508**	**19%**	**15%**
B	"Conditioned"	5.61	8.63	11.03	13.11	**411**		
C	New	3.39	5.37	6.89	8.20	**859**	**13%**	**12%**
C	"Conditioned"	3.92	5.97	7.61	9.02	**751**		
D	New	4.99	7.67	9.95	12.10	**484**	**5%**	**4%**
D	"Conditioned"	5.19	7.93	10.33	12.63	**459**		

Table 4. Thermal Stability Test Data. Results Comparing Measurements at 160 Hours for Sample Set Tested at 86C/50% With Same Sample Set in Same Chamber at 85C/50%.

		Delta E at 160 Hours		
Media	**Method**	**86C**	**85C**	**% Dev**
C	Free Hanging	6.72	5.27	**27%**
D	Free Hanging	5.26	4.90	**7%**
C	Sandwiched w/ C	4.18	3.59	**17%**
D	Sandwiched w/ D	5.42	4.90	**11%**
C	Sandwiched w/ D	5.29	4.61	**15%**
D	Sandwiched w/ C	4.70	4.25	**11%**
C	Sandwiched w/ E	4.57	4.05	**13%**
D	Sandwiched w/ E	4.99	4.52	**10%**

Table 5. Thermal Stability Test Data. Comparing Results of Free Hanging and Sandwich Test Methods on Two Espec ESL-4CW Chambers and One Espec LHU-112 Chamber Tested at 85C/50%.

		Delta E at 640 Hours			Measurement % Deviation	
Media	Method	ESL (1)	ESL (2)	LHU	ESL vs ESL	ESL vs LHU
C	Free Hanging	8.82	9.08	11.89	3%	34%
C	Sandwiched with C	8.35	8.39	8.63	2%	2%
C	Sandwiched with D	9.94	9.95	10.59	1%	6%
C	Sandwiched with E	10.64	10.55	9.62	1%	6%
D	Free Hanging	6.69	6.31	6.92	4%	9%
D	Sandwiched with D	11.80	12.11	11.54	3%	3%
D	Sandwiched with C	8.50	8.71	8.51	3%	1%
D	Sandwiched with E	9.65	9.57	8.89	1%	6%

Table 5 also shows the influence of other media in the thermal test. When Media C was sandwiched with Media D it yellowed more than when it was sandwiched with itself. And conversely when Media D was sandwiched with Media C it yellowed less than when it had been sandwiched with itself. This supported earlier observations that Media D is contributing to its own yellowing (i.e. self contamination).

The introduction of Media E revealed further surprising interactions. For example, sandwiching Media C with Media E caused Media C to yellow more compared to sandwiching with itself while sandwiching Media D with Media E caused it to yellow less compared to sandwiching with itself. It is also not understood why Media C sandwiched with Media D yellowed more in the LHU-112 while Media C sandwiched with Media E yellowed less in the LHU-112 as compared to the ESL-4CW.

Conclusion

This study found that the presence of other samples in the thermal test chamber can significantly influence the results of free hanging samples in the test. Within the small range of possible sample sets explored in this study the results varied by more than 20%. Other combinations of samples could result in greater variation.

To reduce this variation an alternative test method was developed that combines the preferred attributes of the free hanging and sealed bag test methods. The new method sandwiches each test sample between two media sheets of the same type, thereby shielding it from variation in airflow and from contamination due to other samples in the test as in the sealed bag test. The advantages of the sandwich method over the sealed bag method are that it is not necessary to purchase special test bags and that samples may be measured repeatedly rather than discarded after only one measurement.

Testing of the sandwich method confirmed that variation due to contamination was reduced to only 1-3%, as compared to up to 22% variation with free hanging samples. Moreover, the sandwich method also reduced variation compared to that experienced by free hanging samples when using different chambers. One media saw variation between chambers reduced from 34% to 2%.

Not only does the sandwich method reduce test variation, it also more accurately represents actual customer usage. Customers do not usually hang their samples individually in airflow for long term storage. The sandwich method better simulates storage in which image prints are kept stacked together with others of their kind in an album, scrap book, or ‘shoebox’.

Finally, comparing the free hanging results for Media D shown in Table 1 and the sandwiched results for Media D shown in Table 2, shows that the free hanging method can significantly overpredict the image stability of certain media with respect to the enclosed stacked storage condition that the dark storage test method is intended to simulate.

References

[1] 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).

[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 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.