Materials of Construction Test: Insuring the Use of Safe Materials in Photo Books

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Abstract

The photographic industry has had a long-standing concern over the use of materials containing poly vinyl chloride (PVC) materials. This caution was warranted due to PVC materials and plasticizers causing damage to silver halide photographic prints in the 1970s and early 1980s, often from album covers and print storage sleeves, among others. Several international standards for safe storage of photographic materials specifically forbid the use of PVC-containing materials. However, as the photo book industry has grown, new imaging materials are now in use, such as pages produced with electrophotographic printing technologies. In addition the actual materials used in construction of the photo book itself have changed, including the use of modern PVC-containing materials.

Given the historical concerns around the use of PVC, an extensive test was designed to explore a range of modern PVC-containing materials in combination with the typical range of imaging media in use today. This includes silver halide, electrophotographic, inkjet, and thermal dye transfer imaging systems. This paper will review the design, implementation, and results of this test, as well as provide recommendations and test procedures that can be used to determine the compatibility of photo book construction materials with various imaging systems.

Introduction

As the photo book industry continues to grow, so too do the materials used in the construction of photo books. During development of a photo book test method standard [1] concerns were raised by members of the standards development group on the growing use of polyvinyl chloride (PVC)-containing materials in the books. PVC has a troubled history in the photographic industry with many prints destroyed in the mid 70s to mid 80s by plasticizers and hydrochloric acid elution from PVC-containing materials. These materials were typically used as album and enclosure sleeves. During those times, ISO standards covering storage and enclosures [2, 3] were written or revised to forbid the use of any type of PVC material, and rightly so. Since then, the PVC issue has diminished as material producers switched to safer materials such as cellulose acetate and polyester. However, the use of PVC-containing materials began to grow once again as photo book production accelerated. In many cases, however, the materials were a new, modern-generation of materials using high performance plasticizers that were not expected to damage photographic prints. Several members of the ISO development group included photo book producers who wanted the use of PVC to be accepted; it also included members, however, who were from the storage and archiving communities who continued to cite standards that blocked any and all use of PVC. To move the photo book standard forward, it was decided an analytical test method was needed to test the modern PVC-containing materials to insure their safety in photo books. This paper discusses the methodology and results of an extensive test used to form the basis for the Materials of Construction Test to be used on the photo book standard.

Experimental Design

The experimental design necessary to provide the foundation for the proposed Materials of Construction Test included two key variables: a range of PVC-containing materials as well as the range of imaging systems in use today. To study the impact of PVC we needed to include modern materials believed to be free of contamination issues with photographs, and we also wanted to choose materials that were expected to cause problems. Doing so would give us two key results: 1) data to confirm that modern materials would not harm photographic images; 2) data to show damage to photographic images thereby providing a detection mechanism for materials harmful to photographs. Table 1 provides a list of the PVC-containing materials used in the test. The low cost shower curtain was high in plasticizer and was expected to be an excellent material to cause damage to the imaging systems. Two internal and one external controls were also included in the test design: in addition to the PVC-containing materials all imaging samples were tested with polyethylene terephthalate (PET) which is a material known to be safe for storage of photographs. Additionally, all imaging systems were treated under the test conditions without any material in contact with them. Both would provide a means of differentiating colorimetric and physical changes caused by the test conditions versus those caused by the PVC test samples. All imaging systems included a second external control which was held at standard room temperature conditions for comparison to the treated samples.

Table 1- Materials of Construction Samples Tested

Sample ID	Description
1	Leather cover material
4	Matte PVC#1 with low plasticizer
7	Same as 4 but clear
10	Clear PVC#2 low plasticizer level

13	Clear PVC#3 low plasticizer level
16	Clear PVC#4 moderate plasticizer level
19	Clear PVC#5 high plasticizer level
22	PVC shower curtain high plasticizer level
25	PET internal check
28	Blank internal check (no material in contact with image)

Because of the wide range of imaging systems available today for the creation of photo books, we needed to cover these materials in the test plan to determine if certain imaging systems were more sensitive to PVC than others. Table 2 provides a list of the imaging systems used. If a highly sensitive system was found, this would be a good candidate for use as a detector in the Materials of Construction Test.

Table 2 – Imaging Systems

Imaging System	Description
AgX	Chromogenic silver halide photographic paper
Thermal Dye Transfer	Dye diffusion thermal transfer media
Liquid EP	Electrophotographic media with liquid toner
Dry EP	Electrophotographic media with dry toner
Dye on Porous	Dye inkjet on porous media
Pigment on Porous	Pigment inkjet on porous media

As we were looking for both material safety and an imaging detector, our test is broken into two parts: Part 1 aims to show that a range of PVC-containing materials exist that are safe for a wide range, if not all photo imaging systems; Part 2 looks to see if there are one or two imaging systems that are sensitive enough to be considered as a universal detector to determine if a PVC-containing material is safe.

A sensitive test target was also required that would be easy to show and measure degradation caused by PVC and plasticizers. The checkerboard test target from the humidity test method standard, ISO 18946, was chosen [4]. See Figure 1.

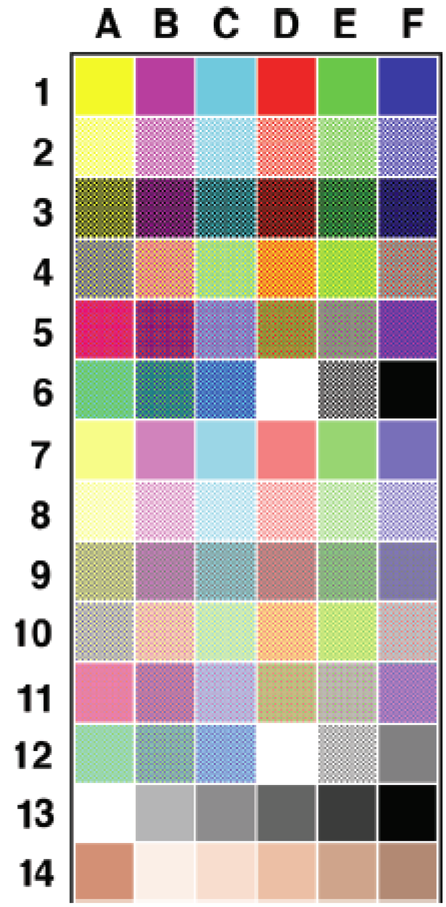

Figure 1 – Checkerboard Test Target

This target is ideal for measuring colorant migration and bleed, which would be encountered with PVC-induced degradation, and contains multiple patches covering both primary and secondary colors as well as both process black (CMY) and pure black (K). The patches are measured colorimetrically before, during and after treatment, and an average delta E calculated to indicate degree of change due to bleed and other factors. The test target and PVC materials were placed in intimate contact, as they would be found in a photo book. In addition, on the silver halide imaging systems, a pH test strip was also included within the sandwich to check for any outgassing of hydrochloric acid, which was a known problem with PVC materials used with silver halide photo systems in the mid 70s and early 80s.

Three treatment conditions were used and covered a wide range of severity, all at 50% relative humidity, to look at test reliability with varying test times. These are summarized in Table 3. The less severe conditions were expected to provide a more sensitive signal, but take a longer time, with the additional benefit of causing less direct thermal damage to the imaging systems.

Table 3 – Treatment Conditions

Condition	Test Duration	Reading Interval	Notes
85 degree Celsius	8 weeks	2, 4, 6, 8 weeks	Ended at 7 weeks
65 degree Celsius	12 weeks	4, 8, 12 weeks	
50 degree Celsius	24 weeks	8, 16, 24 weeks	Extended to 32 weeks

Data Analysis

Colorimetric data analysis was used in this experiment. All 84 patches of the checkerboard test target were measured to determine the change from the external control. A mean and median Delta E value was calculated from all 84 patches of each imaging system for each PVC sample and internal checks. In this test the mean and median delta E values were typically very close to each other. In general, a median delta E is recommended in case a non-normal distribution is encountered, however our analysis used mean delta E to match the analysis required by ISO 18946 humidity test method standard. Figure 2 shows the mean delta E at eight weeks for the 50° C condition with the various PVC samples on the dye on porous imaging system. The delta E is the result of both the test condition and the PVC sample.

To separate out the impact of the test condition on the imaging system from the impact of the PVC, a "delta of delta" was calculated, i.e. subtracting the mean delta E of the conditioned imaging system internal check from the mean delta E of the conditioned system with the PVC sample. Figure 3 shows the delta of delta for the same dye on porous imaging system at 12 weeks of test time.

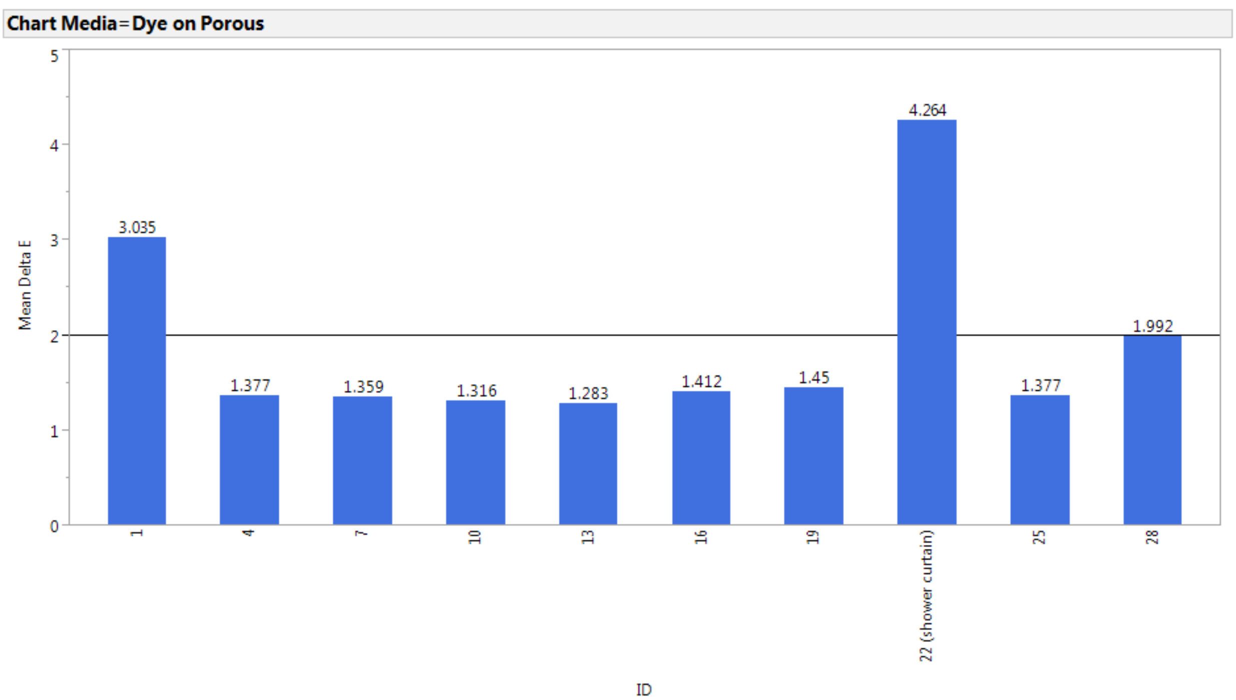

Figure 2 – Mean Delta E for the dye on porous imaging system after eight weeks at 50C/50%RH

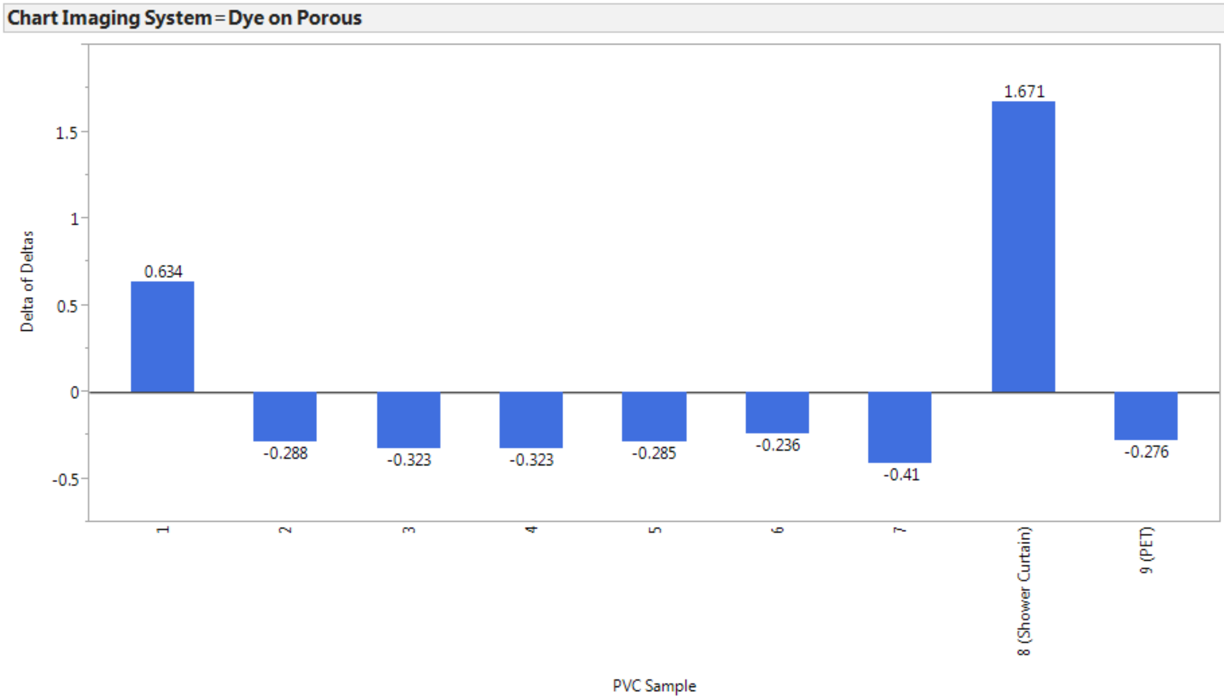

Figure 3 – Mean Delta of Delta E for the dye on porous imaging system after 12 weeks at 50C/50%RH

Results and Conclusions

Test conditions

The 85 degree test condition was quickly determined to be too harsh. As expected, there was significant colorant migration with the thermal dye transfer system due to its low glass transition temperature. Unexpected, however, was the significant damage of the PVC samples themselves. Most were severely yellowed, although the degree of yellowing was inversely related to the assumed level of plasticizer. See Figure 4.

We assume that the severe temperature caused a loss of plasticizer in the PVC samples resulting in the yellowing. Using the internal (PET) and external checks to subtract out the temperature effect, there was little differentiation among the PVC samples with most of the imaging systems, with the exception of the shower curtain and leather book cover material. Additionally, nearly all the pH test strips were destroyed by the heat. Finally, several systems could not be analyzed because of blocking of the image with the PVC sample. Our conclusion is that the 85C/50%RH test is too severe for use as a test method, and we actually ended this test one week earlier than planned.

The 65C/50%RH test condition also showed the expected colorant migration issues with the thermal dye transfer imaging system, but it did not show the severe changes in the PVC samples that was seen with the 85° C test. However, there also was not much differentiation among the PVC samples by the various imaging systems, with all samples degrading to a similar degree, even after the full 12 week test time.

The 50C/50%RH test condition provided the best combination of minimizing external, non-PVC damage to the imaging systems and more significant differentiation among the PVC samples. An anticipated drawback of this condition was the need for a long test time.

Figure 4 – Degradation of PVC samples after seven weeks at 85C/50%RH

This test condition was run to 32 weeks, eight weeks longer than planned. Interestingly, in the case of the more damaging PVC materials with sensitive imaging systems the test can be run for as little as eight weeks. See Figure 5 which shows the delta E change for all the PVC samples from the internal check over time for the thermal dye transfer imaging system.

The 50C/50%RH test condition does a very good job of differentiating poor PVC samples from good. Referring to Figures 2 and 3 above it is clear that Samples 1 and 22 are showing more change than the others in as little as eight weeks (Figure 2). This differentiation was maintained at 12 weeks (Figure 3) and was confirmed all the way to the end of the test at 32 weeks. See Figure 6, which shows the impact of Sample 1 on the thermal dye transfer system. Note that because of blocking early in the test, the data on Sample 22 (shower curtain) was lost.

The overall conclusion for the test conditions is that the 50C/50%RH test is the best for differentiation of PVC materials. When used as a pass-fail test, it can be run for as little as 8-10 weeks.

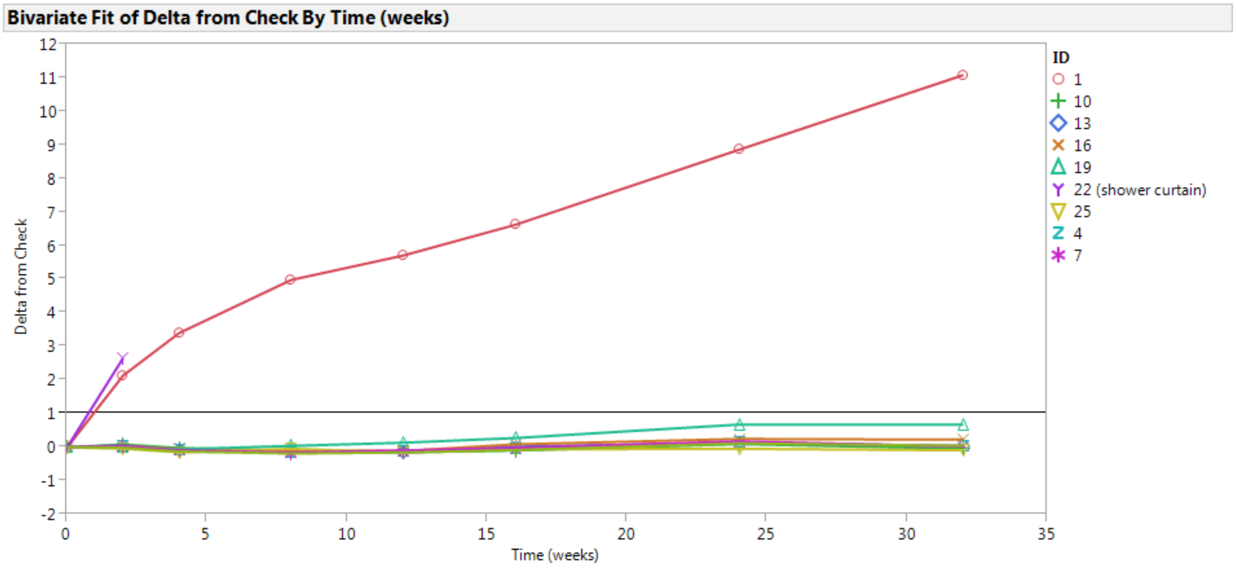

Figure 5 – delta E for all the PVC samples from the internal check over time for the thermal dye transfer imaging system at 50C/50%RH

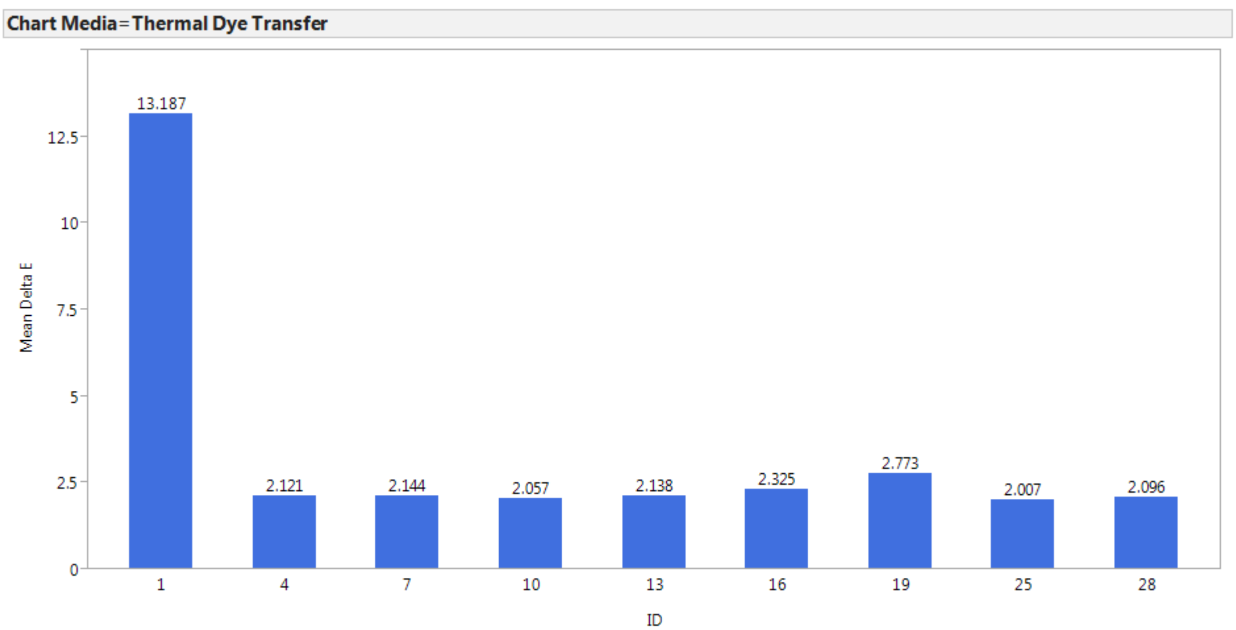

Figure 6 – Mean Delta E for the thermal dye transfer imaging system after 32 weeks at 50C/50%RH

Safety of PVC Materials

Based on both the 65° C and 50° C test conditions, all the PVC-containing materials tested, with the exception of the leather book cover material (Sample 1) and the shower curtain (Sample 22) were safe for all the imaging systems in the test plan. Hydrochloric acid outgassing and plasticizer exudation, both common problems with photo albums in the late 70s and early 80s, were not found in this test. The pH strips included with the AgX imaging system showed no significant change in the 50 and 65° C conditions (and were destroyed in the 85° C condition). Visual examination of the test targets showed no signs of physical degradation due to the plasticizers in any of the conditions including 85° C. Research into these PVC-containing materials (Samples 4-19) indicate they are of a new class of "rigid" PVC films with very slow decomposition at elevated temperatures (120-150° C) and virtually none at room temperature. This is borne out by the minimal impact on the imaging systems in this test. See Figures 7-8, showing delta of delta in the 50° C test condition at 32 weeks with the thermal and dye on porous imaging systems, both of which showed sensitivity only to Samples 1 and 22.

These data clearly indicate that there are modern PVC-containing materials that are very safe for photographic applications using all imaging systems tested. This conclusion has been accepted by the ISO committee, allowing the development of the standard to proceed despite earlier storage standards that forbid the use of PVC -containing materials in photographic applications. To illustrate the low sensitivity of the imaging systems see Figure 9 and 10, which show the mean delta E of the liquid EP and AgX imaging systems respectively. Of all the imaging systems with the exception of thermal and dye on porous, liquid EP showed the lowest sensitivity and AgX the highest sensitivity of the various imaging systems to the modern PVC materials. Note the expanded scale of these plots. Both figures are from the 50° C test condition at 32 weeks. Similar lack of sensitivity was seen in the 65° C and 85° C conditions.

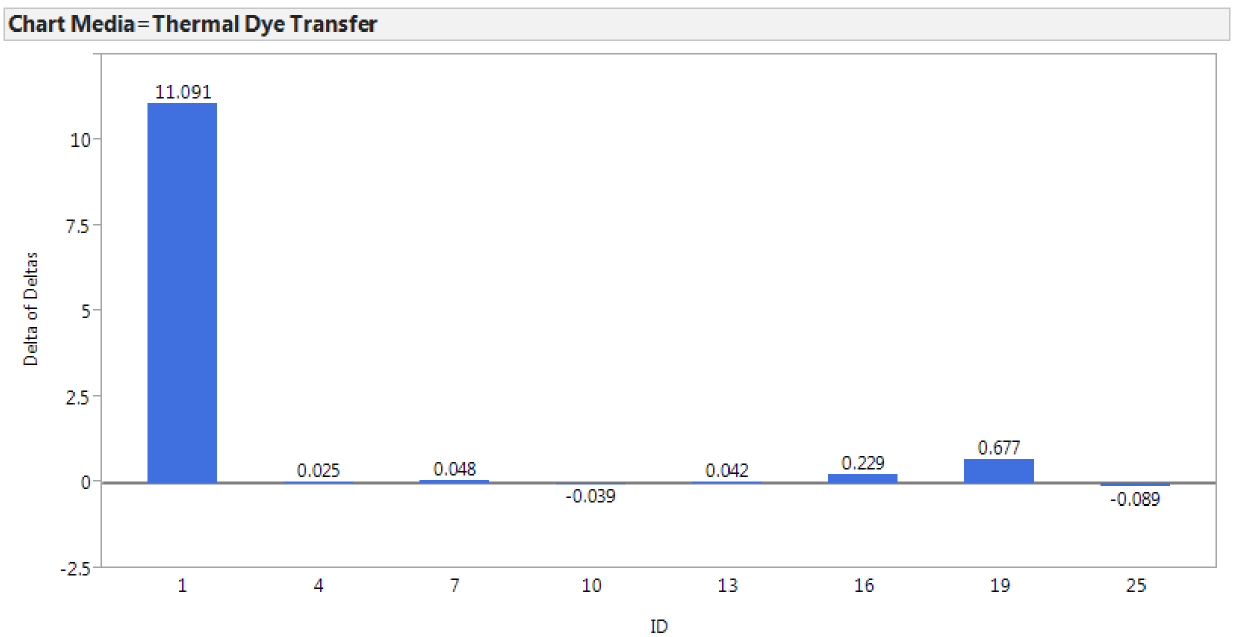

Figure 7 – Delta of mean Delta E for the thermal dye transfer imaging system after 32 weeks at 50C/50%RH

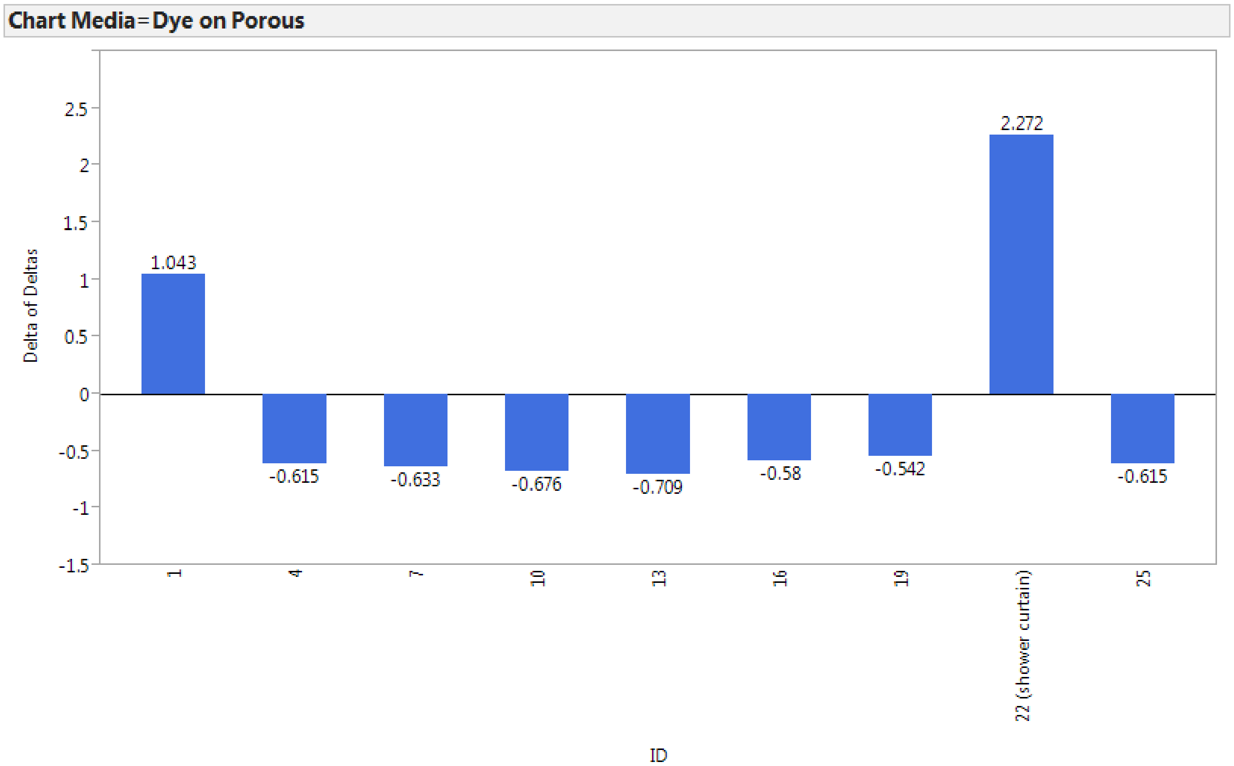

Figure 8 – Delta of mean Delta E for the dye on porous imaging system after 32 weeks at 50C/50%RH

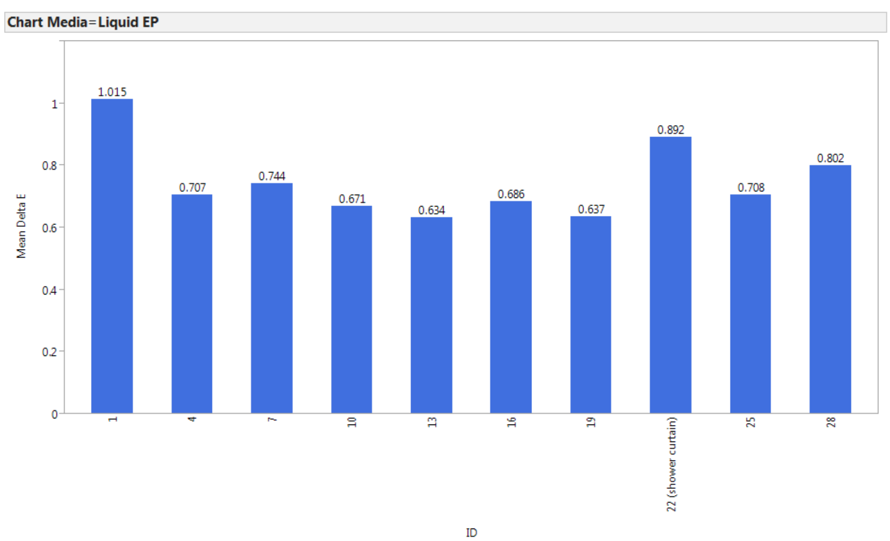

Figure 9 – Mean Delta E for the liquid EP imaging system after 32 weeks at 50C/50%RH

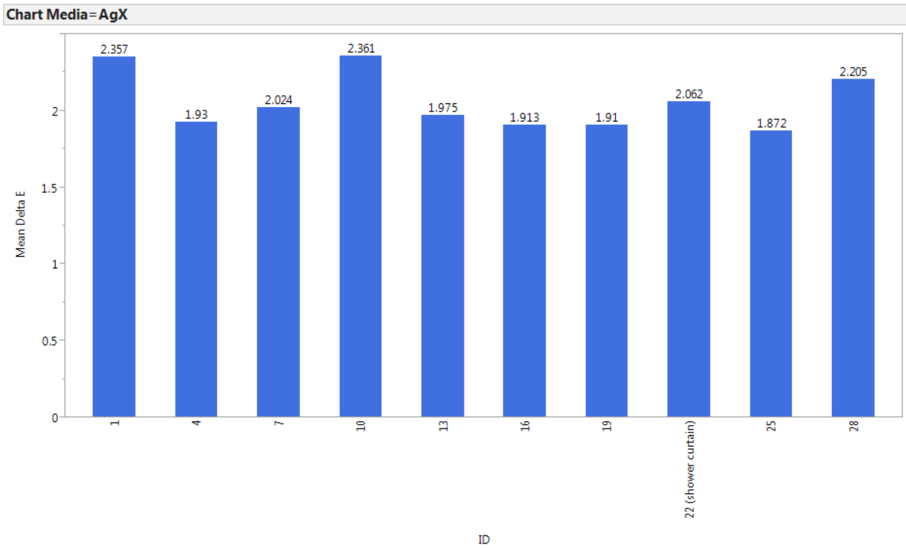

Figure 10 – Mean Delta E for the silver halide imaging system after 32 weeks at 50C/50%RH

Imaging Systems as Sensitometric Detectors

Of the six imaging systems used as targets, the thermal dye transfer and dye on porous systems showed the most sensitivity to the PVC-containing samples. Note the large delta E change with Samples 1 and especially 22 (shower curtain) on the dye on porous media in Figure 11, and the very large delta E change with Sample 1 (leather cover material) on the thermal dye transfer media (see Figure 6). In Figure 12, one can easily see the deterioration of the test target compared to the check. Because of severe blocking that occurred early in the test, data from the shower curtain (Sample 22) on the thermal media is not available. Both figures are from the 50º C test condition at 32 weeks. Similar differentiation was seen in the 65º C and 85º C conditions.

A simplified way to illustrate the sensitivity of the imaging systems as detectors is to look at all imaging systems on the two most troublesome PVC samples, Samples 1 (book cover) and 22 (shower curtain). Figure 13 shows the 50º C 32 weeks delta from the external check for all imaging systems with Sample 1 (leather book cover material) and PET. Clearly the thermal dye transfer system is much more sensitive than the others.

Figure 14 shows the same conditions and analysis for the shower curtain. Additionally, it also shows that the pigment on porous imaging system was quite sensitive to the shower curtain material.

Data on the thermal system were not available due to blocking. Had it not been for the blocking we would have expected to see a very strong signal with thermal as well.

Conversely, the other imaging systems were limited in their differentiation among the PVC samples and would make generally poor sensitometric detectors. See Figures 9 and 10, shown earlier, which show the lack of PVC sample differentiation with the liquid EP and AgX imaging systems, respectively.

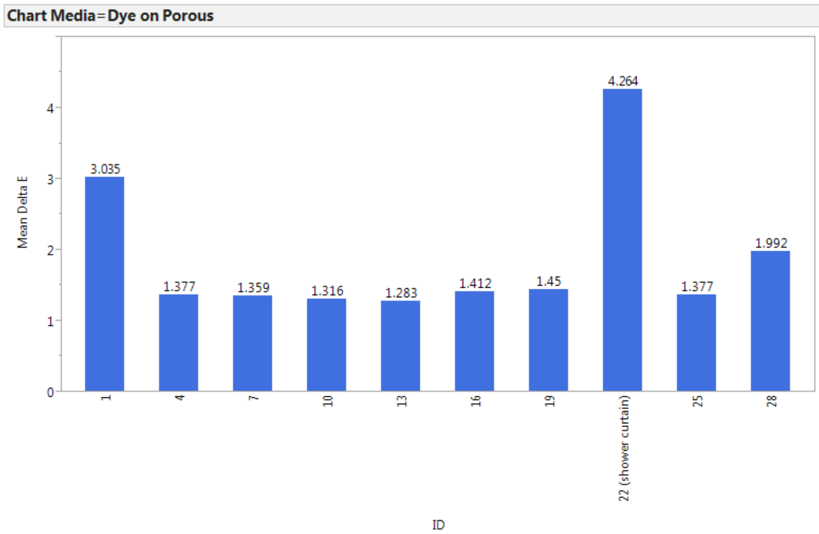

Figure 11 – Mean Delta E for the dye on porous imaging system after 32 weeks at 50C/50%RH

Figure 12 – Visual impact of Sample 1 on the thermal imaging system

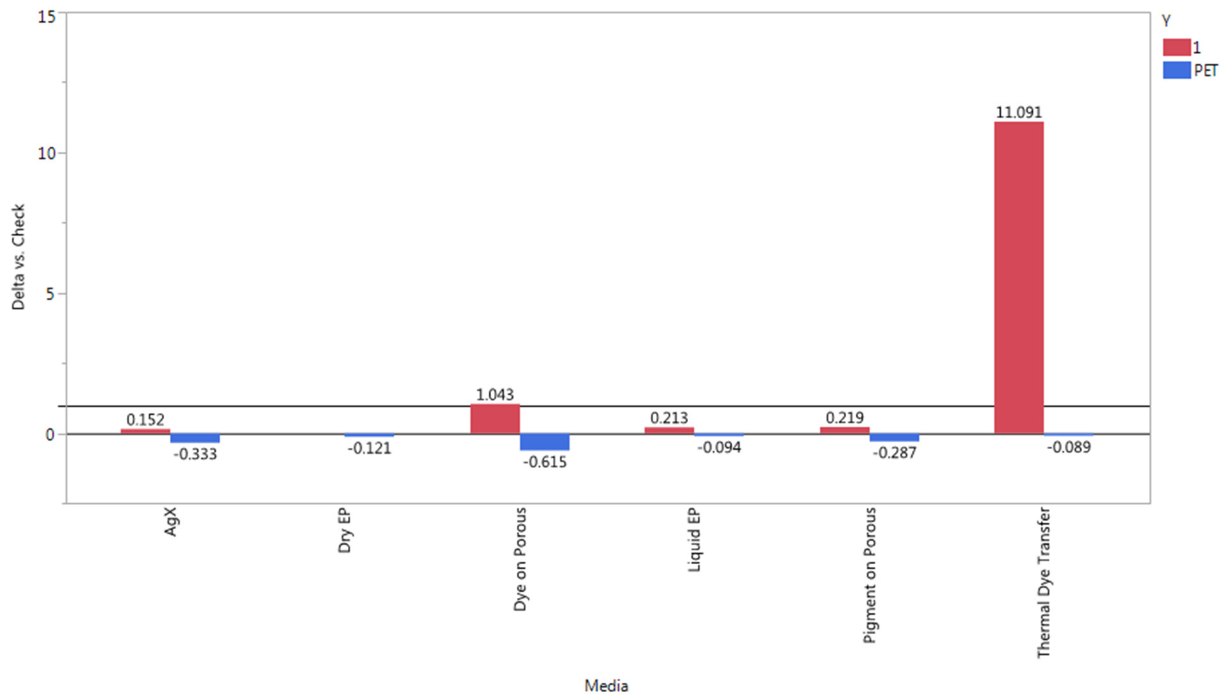

Figure 13 – Mean Delta E delta from external check of Sample 1 on all imaging systems

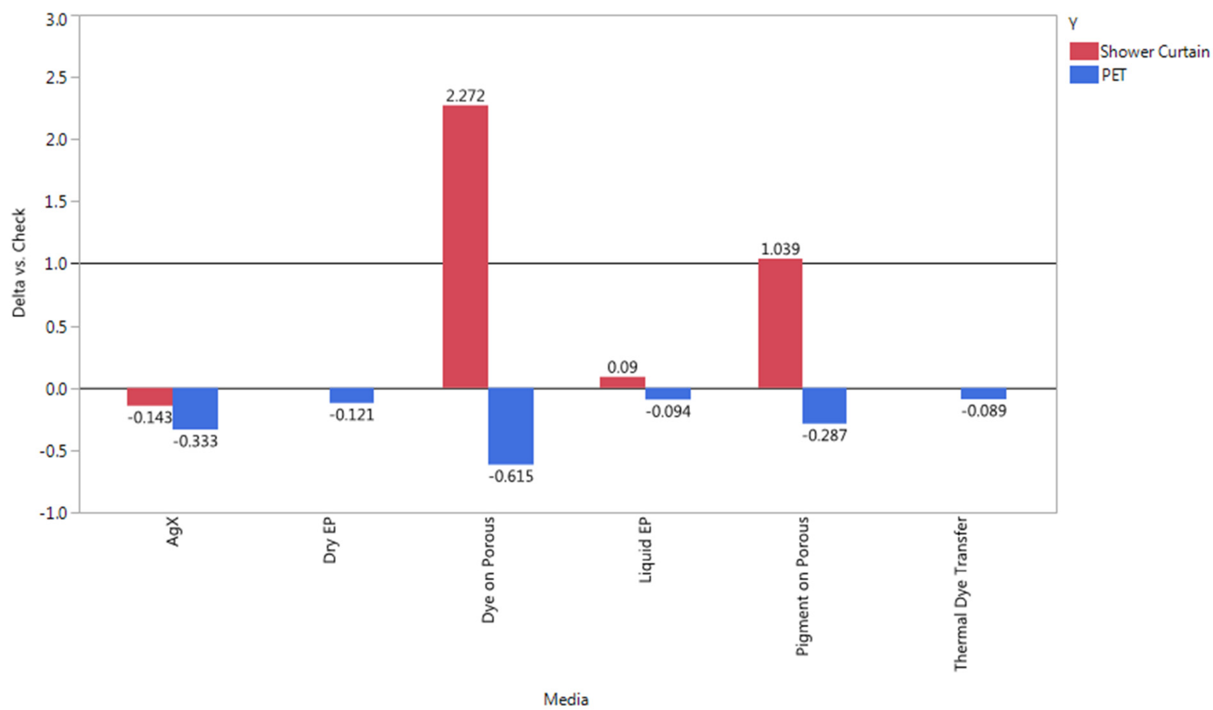

Figure 14 – Mean Delta E delta from external check of Sample 22 on all imaging systems

Imaging Systems as Physical Detectors

We have mentioned several times that the shower curtain caused blocking early in the test conditions with the thermal dye transfer imaging system. The dry EP imaging system also had several instances of blocking early in the testing with both Sample 22 (shower curtain) and Sample 1 (book cover material). Therefore the best imaging systems as detectors of physical issues are the thermal and dry EP systems, with both showing blocking in as little as two weeks test time.

A Test for More than PVC

Further research into the issues being caused by the book cover material indicate these issues were not PVC related but instead linked to the tanning agents used in the leather. This reinforces the concept that the testing and analysis conducted here can be broadened into a more general test for safety of various materials to be used in photo books as opposed to just a PVC test. Hence the broadened title of "Materials of Construction" test, rather than a PVC test. It should also be noted that while the leather book cover material was problematic when in intimate contact with the image it did not show any indications of causing problems (such as due to outgassing) when the material was not in contact with the imaging systems.

Conclusions – Proposal for a Test Protocol

Based on the results of this study, we are proposing two test protocols, one standard and one simplified, based on the specific needs of the user. The standard protocol would be used in cases where the user needs to determine the safety of various materials of construction on various imaging systems. This is directly related to the experiment reported here. The simplified protocol would be used in cases where the user produces photo books with one imaging system and limited materials of construction.

Standard Protocol

The standard protocol makes use of two test procedures, a pass-fail test looking for physical deterioration such as blocking, followed by a sensitometric test to look for damage to the imaging system caused by colorant migration. By doing the short term pass-fail physical deterioration test first, early elimination of proposed materials of construction can take place before running the longer term sensitometric test.

Our experiment showed that dry EP and thermal dye transfer were the imaging systems most prone to blocking, therefore both systems should be used as detectors in the physical deterioration test. Only a simple imaged target is needed consisting of eight colorant patches: cyan, magenta, yellow, red, green, blue, process neutral (CMY) and neutral (K), plus an area of D-min. The more complex checkerboard target that was used in our experiment can be used but is not required. The test condition is 50C/50% RH for two weeks. Construction materials that exhibit blocking fail and are eliminated; those that pass proceed to the sensitometric test procedure. Failure of either one of the detectors is failure for that particular material of construction.

Our experiments showed that dye inkjet on porous media and thermal dye transfer were the imaging systems most sensitive to colorant migration and therefore both systems should be used as detectors in the sensitometric test. A checkerboard test target is required using mean delta E analysis, with materials of construction placed in contact with the targets. For comparison (internal control) a second set of test targets are conditioned with no material in contact. As a secondary control, PET in contact with the test targets can be used. The test condition is 50C/50% RH for eight weeks. Based on multiple studies on colorant migration due to various conditions (for example high humidity) a very stringent delta E of 1.0 is used to determine if a construction material passes or fails [5]. 1.0 was chosen because of the very poor performance of PVC materials in photo albums, and wanting to minimize chances of similar issues with modern systems. A slightly less stringent delta E could be considered. As done in our experiment, the delta E to determine failure is measured as the "delta of delta", i.e., the mean delta E of the test material compared to the mean delta E of the control.

The standard protocol, using three imaging systems and testing for both physical and sensitometric deterioration, provides a very stringent test for determining if a material of construction is safe for use in photo books produced by any of the typical digital imaging systems in use today. With the very tight delta E limit the chance for a false positive, that is passing a material when it should fail, is very low. The standard protocol also protects against false negatives by using three imaging systems as detectors.

Simplified Protocol

In the case of photo books produced with one imaging system, with perhaps a limited interest in only one or two materials of construction, the simplified test protocol eliminates much of the preparation and analysis time of the standard protocol. In this test protocol the pass-fail physical deterioration test is run if the imaging system to be used in the photo book production is either dry EP or thermal dye transfer. If a different imaging system is to be used, the physical deterioration test with dry EP and/or thermal should still be considered as the other imaging systems tend to be less sensitive to deterioration. As in the standard protocol, the checkerboard target is used to measure colorant migration with the same delta of delta analysis and failure points as above. However, the only imaging system used in this protocol is the one being used for photo book production.

Overall conclusion

Either the standard test protocol or the simplified protocol provides a means of screening materials of photo book construction that will conclusively determine the safety, or lack of safety for use in photo book applications. These tests could also more broadly be extended to photographic applications, such as storage sleeves and other storage materials, beyond the photo book application. Ultimately, the goal is the safe use and long term preservation of photographs with modern digital imaging systems.

Acknowledgements

The authors would like to thank Kodak Alaris and the personnel of the Kodak Alaris Image Stability Technical Center for the conditioning time in their chambers as well as the handling, reading, and analysis of the test targets. The authors would also like to thank Mr. Guido Peleman of Peleman Industries and Mr. Dirk Peereboom of BN International for providing materials of construction test samples. Finally, the authors would like to thank Dr. Jon Kapecki for his technical and editorial support and encouragement over many years.

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[3] ISO 18920:2011 – Imaging materials – Reflection prints – Storage practices

[4] ISO 18946:2011 – Imaging materials – Reflection colour photographic prints – Method for testing humidity fastness

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Author Biography

Joseph LaBarca is a 19-year member of the ISO Technical Committee on Photography and is directly involved in the ANSI/IT-9 and ISO Working Group 5 Committees on color print stability and physical properties. After retiring from Eastman Kodak Company with over 34 years of continuous service Joe formed JEL Imaging Services in 2010 and Pixel Preservation International in early 2011, to provide consulting services to the imaging industry on image preservation, ISO standards, and image quality. He is a graduate of Bucknell University with a Bachelor's of Science Degree in Chemical Engineering and spent a large part of his career at Kodak in the research, development, and commercialization processes for Kodak Ektacolor papers and processing chemistry. This included extensive involvement in the image stability of color papers beginning in the early 1980s and continuing for the remainder of his career at Kodak. In 2004 Joe assumed the role of Technical Director, Image Permanence with responsibilities that included silver halide, inkjet, thermal dye transfer, and electrophotographic imaging systems. Joe has been a member of IS&T for over 28 years and was awarded Senior Membership in 2012. He has also been a member of the American Institute for Conservation since 2008.