Investigations into Potential Reactivity between Silver-Halide and Digitally Printed Photographic Images in Long-Term Storage

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Abstract

The purpose of this project was to investigate the possibility that digital prints, i.e., electrophotographic, inkjet, and dye sublimation, stored in direct contact with silver-halide prints in mixed collections will cause accelerated degradation of the silver-halide prints. It cannot be assumed that these prints will be chemically compatible during long-term keeping. Since consumer collections of printed images may contain mixtures of both digital and traditional photographs, it is important that they do not adversely interact with one another. The method outlined in ISO 18916 Imaging Materials—Processed Imaging Materials—Photographic Activity Test for Enclosure Materials *was used to predict potentially harmful interactions between these print types. Some digital prints were reactive with silver-halide prints while others were not. The fact that some digital print materials could degrade adjacent materials also suggests that their own chemical compositions are unstable in ways not previously identified; thus, results from this project should be useful for manufacturers looking to improve the formulations of their products.*

Introduction

The purpose of this project was to investigate the possibility that digital prints stored in contact with traditional prints may cause accelerated chemical degradation of the traditional prints. It cannot be assumed that both types of imaging systems are chemically compatible during long-term keeping. Users may bring the two types of materials into close proximity for extended periods, because they wish to mix prints based on content, or because they have a limited storage area. It is important that these materials do not interact adversely with one another over time.

This project was limited to predicting damage to traditional photographs caused by digital prints. It did not examine whether traditional photographs might harm digital prints or whether the different digital printing technologies (e.g., electrophotographic and inkjet) might be harmful to each other. Additionally, the project did not test for physical interactions such as blocking, ferrotyping, colorant transfer, or abrasion. The project evaluated digitally printed text documents in addition to pictorial print systems, because text documents may be intermixed with photographs in enclosures or placed with traditional prints in albums or scrapbooks.

It is already well known that some collection materials should not be stored in close proximity with certain others (nitrate and acetate films, for example). These may be different types of materials or the same material at different stages of deterioration [1]. However, there are no known published studies examining potentially harmful effects of storing digital and traditional prints together. There are also no known cases of such damage occurring in real collections. This does not lessen the importance of the work however, as preliminary accelerated-aging test results did indicate a potential problem. This sort of damage would occur in real life over decades, and since digital printing is relatively new, it is likely that such damage has not had enough time to appear.

Methods

The photographic activity test (or PAT) of ISO Standard 18916 [2] was chosen as the basis for the method of investigation. It is an existing, well-established test for predicting long-term interactions between photo-storage materials and photographs. In this project the photo-storage materials were replaced by digital print materials to screen for possible harmful interactions between them and traditional silver-halide photographs.

The PAT uses two detectors to simulate a silver-halide photographic image. The first, called the image interaction detector, consists of colloidal silver particles distributed throughout a gelatin coating on clear polyester film (despite the fact that the test uses silver in its detector, it is permissible to extrapolate the test results to chromogenic prints which use dyes). This detector is used to predict oxidation and reduction reactions between the test materials and traditional photographs. These reactions would eventually result in fading (oxidation), mirroring, and red spots (oxidation and reduction) in actual materials during long-term storage. The second, called the gelatin stain detector, is a strip of white, processed photographic paper. This detector is used to predict discolorations (such as yellowing) of the gelatin binder. Premium-weight black-and-white photo paper is used because its thick gelatin layer is very sensitive to staining. The PAT has been benchmarked against known reactive and inert enclosures from real collections and as such provided accurate predictions of whether digital prints will adversely react with traditional prints during extended-term storage.

A variety of ingredients are used in the manufacture of digital printing papers and colorants. The goal of this project was not to determine what specific ingredient of the paper or colorant, if any, could cause harmful reactions with traditional photos but was simply to determine whether there would be any reactions at all. Still, it was worthwhile to separately test printed images and unprinted papers.

A total of 15 different unprinted papers were tested from the following groups: inkjet specialty photo (both porous and polymer), inkjet fine art, dye sublimation (printed to Dmin to include overcoat), chromogenic (processed to Dmin), and coated digital press. Several examples from each type were tested when possible.

To test the colorants, a total of 13 different printed digital photographs were selected from the following groups: inkjet pigment, inkjet dye, dye sublimation, chromogenic, and digital press. The printed photograph samples consisted of uniform areas of sRGB 128, 128, 128 to create mid-tone, process gray. All of the inkjet samples were printed on the same paper (plain white office), which had passed in the paper-only tests. This was done to ensure that the paper did not contribute to, and thus confound, any colorant test failure results. Several examples of each type were tested when possible.

The digitally printed text document materials were tested in the same manner as the pictorial images. There were 10 unprinted papers and 14 printed text documents. With the exception of offset, all of the samples were printed on the same paper (plain white office), which had passed in the paper-only tests. This was done to ensure that the paper did not contribute to, and thus confound, any colorant test failure results. The offset was printed on coated glossy stock.

The papers and prints were cut into 2cm x 4cm strips. Each material was incubated against two image interaction detectors and two gelatin stain detectors in each test. All tests were performed three times and the results averaged. The materials were stacked into a specimen jig in the following configuration:

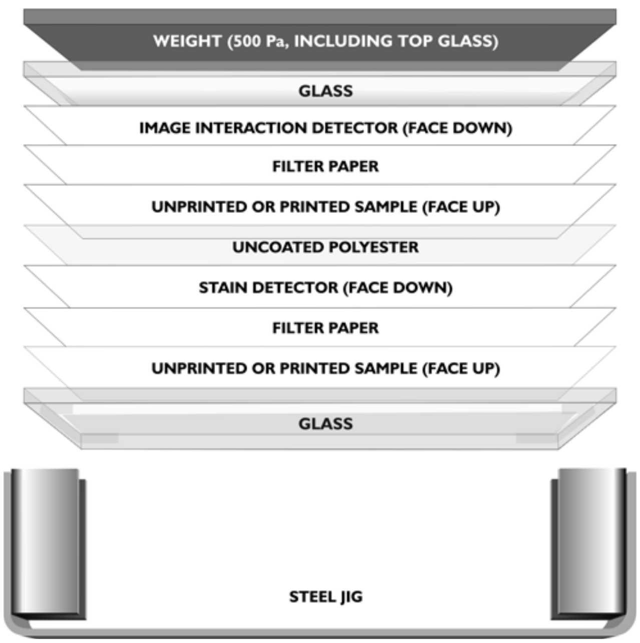

Figure 1. *Arrangement of materials in the test jig.*

As shown in Figure 1, pieces of Whatman No. 1 filter paper separated the digital print materials from the detectors. These filter paper separators are included to prevent confounding physical interactions that sometimes occur in the test. This use of filter paper is described in the ISO standard. In this project, the filter paper could perform the additional function of preventing potential dye migration from the digital photographs onto the detectors, which would confound the measurements.

The prepared jigs were placed in the incubation chamber on wire racks with sufficient space between them to allow for air circulation. The tests were incubated in ESPEC LHL-112 Humidity Cabinets at 70 C and 86% RH for 15 days. The authors were aware that such extreme conditions could result in dye bleed for some of the digital prints; however, since the goal of the project was not to evaluate damage to the digital prints but to the traditional prints, and since the location of the colorant on the print was not considered vital, the method was used as described in the ISO standard. Testing at lower temperatures and humidities could have resulted in untenable test times of several years, as opposed to weeks.

The detector strips were measured using an X-rite 310 densitometer at four locations on each strip, using Status A blue diffuse density both before and after incubation. The after-incubation measurements were made at approximately the same locations as the before-incubation measurements. Status A blue density was used as it is the most sensitive to changes in the detectors. Transmission density was measured on the image interaction detector, and reflection density was measured on the gelatin stain detector.

The PAT requires the use of a control, which is also Whatman No. 1 filter paper. This paper is assumed inert with respect to photographs and acts as a “known good” material to which the digital print materials will be compared. The control is incubated at the same time as the test materials and against the same type of detectors. Pass/fail limits for the test are based on the change in density of the control detectors. The PAT is a pass/fail test that requires that all three of the following sub-tests are passed to satisfy an overall pass rating: image interaction, mottling, and gelatin staining. The final results are reported as pass/fail for each unprinted paper and each printed paper.

Image Interaction

Using the following equation, the percent difference between the density change of the detectors in contact with the unprinted paper or digital photograph and the density change of the detector in contact with the control can be calculated:

$$X\% = \frac{(\Delta Ds - \Delta Dc)}{\Delta Dc} \times 100$$

where X is the percent difference between the control and test material detector changes, ΔDs is the density change of the sample detector, and ΔDc is the density change of the control detector.

In order to pass the image interaction portion of the PAT, the digital print material should not produce a percentage change greater than ±20% of the control.

Mottling

The test material should also not produce *easily recognizable* mottling of the image interaction detector for the test material. Mottling is defined as localized, non-uniform visual density variation [3]. This is a subjective visual assessment.

Gelatin Stain

For the gelatin stain test, the density of the digital print material detector should not be greater than 0.08 over the density of the control detector.

Results and Discussion

Digitally Printed Photos Stored with Traditional Photos

None of the photo papers or colorants caused gelatin staining or mottling. Some of the papers and colorants reacted with the image interaction detectors. Tables 1 and 2 show the pass/fail image interaction results for the various papers and printed photographs.

Table 1: Photo Papers

Paper Type	Result
Inkjet photo paper – porous – glossy	Pass
Inkjet photo paper – porous – glossy	Pass
Inkjet photo paper – porous – glossy	Pass
Inkjet photo paper – polymer – glossy	Pass
Inkjet photo paper – polymer – glossy	Pass
Inkjet fine art paper – porous – matte	Fail
Inkjet fine art paper – porous – matte	Pass
Inkjet fine art paper – porous – matte	Pass
Inkjet fine art paper – porous – matte	Pass
Dye sublimation paper – glossy	Pass
Dye sublimation paper – glossy	Pass
Color silver halide – glossy	Pass
Digital press – coated glossy	Pass
Digital press – coated matte	Pass
Digital press – uncoated	Pass

Table 2: Photo Colorants

Printer Type	Paper	Result
Inkjet - pigment	Plain office	Fail
Inkjet - pigment	Plain office	Pass
Inkjet - pigment	Plain office	Pass
Inkjet – dye	Plain office	Pass
Inkjet – dye	Plain office	Pass
Inkjet – dye	Plain office	Pass
Dye sublimation	Dye sublimation	Pass
Dye sublimation	Dye sublimation	Fail
Dye sublimation	Dye sublimation	Pass
Silver halide	Chromogenic	Pass
Digital press – liquid toner	Coated glossy	Pass
Digital press – dry toner	Coated glossy	Pass
Digital press – dry toner	Coated glossy	Pass

Overall, 6% of the papers and 15% of the colorants failed the test. Two of the test materials that failed—the inkjet pigment (Table 2) and the inkjet fine art paper (Table 1), which is typically used with pigment printers—are also extremely sensitive to abrasion; for this reason alone, they should not be stored in contact with traditional photos or any other type of print. The test results for the dye sublimation colorant that failed varied widely from run to run. The dye also bled heavily to the verso side of the substrate, though it did not bleed across to the test detector. This is potentially an anomalous effect, which should be more fully understood before being used to suggest that dye sublimation or all digital prints be stored away from traditional prints, especially since the substrate for this material passed. Given the low rate of failures, it is therefore probably safe to allow storage of digital photos with traditional photos as long as they are physically durable enough to resist abrasion and are kept at appropriate storage temperature and humidity levels (maximum 25°C and between 20% and 50% RH [4]).

Digitally Printed Text Documents Stored With Traditional Photos

None of the text document papers or colorants caused gelatin staining or mottling. Several of the papers caused oxidation (fading) of the image interaction detector (see Table 3); however, none of the colorants caused such damage.

Table 3: Text Document Papers

Paper Type	Result
Inkjet-specific document paper	Fail
Inkjet-specific document paper	Fail
Inkjet-specific document paper	Fail
Electrophotographic-specific paper	Pass
Color electrophotographic-specific paper	Fail
Office paper – virgin pulp	Pass
Office paper – 50% recycled content	Fail
Office paper – 100% recycled content	Fail
Offset lithographic – coated glossy	Pass
Offset lithographic – coated matte	Pass
Offset lithographic – uncoated	Pass

While all of the colorants passed the test, 55% of the papers failed. All of the inkjet-specific document papers failed the test. It is not known what component of these materials caused these harmful reactions. Therefore, documents printed with these products should not be stored with traditional photos until the problem is understood and overcome. The electrophotographic papers were split in their reactivity. Those made from recycled papers failed and should not be intermixed with traditional photos. It has already been determined that enclosures made of recycled papers should not be used as storage enclosures due to the potential for damage [5]. Many recycled papers include groundwood, which is known to cause degradation of photographic images [6]. It seems clear, then, that prints made using recycled papers or any other paper containing groundwood should not be stored in close proximity to traditional photographs.

Three offset papers were tested, and all passed the test; however, there is a large variety of these papers on the market. Any offset prints made on recycled or groundwood papers also should not be mixed with traditional photos.

It is clear that the risk of storing printed documents in contact with traditional prints is high. Digitally printed documents and traditional photographs should be segregated; however, it may be possible to minimize the potential for interaction damage by placing either the photos or the documents, or both, individually in plastic sleeves [7].

Conclusions

Digitally printed photographs may be stored with traditional photographs if the digital prints are resistant to abrasion and the materials are kept in appropriate storage conditions.
Digitally printed text documents should be segregated from traditional photographs or placed in appropriate plastic sleeving [5].

Finally, if some digital print materials (photos or text documents) are harmful to traditional photos, they may also be reactive with each other or even be auto-destructive (generating their own degradation reactants). Manufacturers of these products should look for these causes and adjust product formulations as necessary.

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