Colorant Fade and Page Yellowing of Bound and Unbound Materials Printed Using Digital Presses and Offset Lithography when Exposed to O₃ or NO₂

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Abstract

The printing industry has seen growth in the number of bound digitally-printed materials since the introduction of commercial digital presses. Many short-run publications, such as research monographs, periodicals, and books have already entered the collections of cultural heritage institutions. It is vital that information be made available regarding the care of these materials. There is no known previous research on the effects of pollutants, such as O₃ (ozone) or NO₂ (nitrogen dioxide), on bound digitally-printed materials. This study was undertaken to specifically investigate the susceptibility of digital press and offset printed bound materials to page yellowing and colorant change when exposed to O₃ and NO₂ independently. The research findings demonstrated that bound digitally-printed materials are at risk to damage by these airborne pollutants. Cultural heritage institutions that have these materials within their collections should take precautions to mitigate deterioration through the use of air filtration, reduced temperature storage, or low permeability enclosures. The method chosen should match the use and size of the collection and the resources of the institution.

Introduction

Offset lithography dominated the commercial printing market for the past 50 years and now high-speed electrophotographic and inkjet digital press systems are changing the market [1]. The print quality of digital presses has been improving and it has more application capabilities and short-run capabilities, than offset lithography [2]. Digital press systems also provide versatility in terms of the wide range of substrates on which they can print [3]. However, the permanence issues with bound materials created by digital presses have yet to be fully investigated.

The permanence of bound digitally-printed materials is vital because they already exist in collections. According to Wilhelm, the images in photobooks are as valuable as traditional silver-halide photographs, since the majority of them are not produced in any other hardcopy form [4]. The greatest concerns with regards to the permanence of bound digitally-printed materials are the yellowing of the pages over time and the potential for colorant fade. Although books most often remained closed and stored on bookshelves, the cover might be susceptible to fade, or if the book is opened and displayed on a table, then the pages might be susceptible to fade [4]. The book bindings are also an important factor; however, the durability of bindings will not be covered in this paper. This paper is the first published research on the sensitivities of digitally printed bound materials to O₃ or NO₂ exposure.

Methodology

Bound and Unbound Materials

The bound materials were printed using three different digital press systems (dry-toner electrophotography (EP), liquid-toner EP, pigment inkjet) and offset lithography. Except for the pigment inkjet prints, the sheets were bound in three different configurations: stitched-hardcover book, glued-softcover book, and stapled periodical. Each binding type was paired with a specific paper (hardcover with uncoated paper, softcover with glossy paper, stapled periodical with glossy paper containing 30% recycled content) commonly used with each type of binding. The pigment inkjet prints, which used a glossy inkjet-primed paper, were only bound as stapled periodicals.

Unbound sheets from the sample set were also tested to compare the effect of pollutants on free-hanging samples versus samples in bound form. Table 1 shows printing technology, paper type, binding type, and sample codes used in this experiment. Note that DP stands for “digital press.”

Test Targets

The bound pages contained printed test targets to quantify the yellowing and colorant fade that resulted from the pollutant exposure. The following test elements were included on each page spread (see Figure 1):

- Edge yellowing was assessed using paper measurements at positions indicated by arrows at the paper corners, along the edges (including the gutter), and in the center of page
- Colorant fade was evaluated using Dmax (maximum density) CMYK (13mm x 26mm) patches
- Two pictorial images and a text target for illustrative purposes
- A 73-patch color target was cut out and used for the unbound free-hanging portion of the experiment. This target included cyan, magenta, yellow, red, green, blue, and neutral ten-step tint ladders, as well as a white (non-printed) patch used to measure paper yellowing. Only Dmax CMYK and a white patch data will be reported in this paper.

Measurements

Color change and page edge yellowing were measured using a GretagMacbeth Spectrolino/Spectroscan (D50, 2° Observer, with the UV component included). CIELAB values were collected for both pre- and post-pollutant exposures to calculate ΔE*ab. The bound volume measurements were made from pages located at the beginning, middle, and near the end of the book using a white backing material. All test samples were conditioned...
Table 1. Materials Tested.

<table>
<thead>
<tr>
<th>Printing Technology</th>
<th>Paper</th>
<th>Binding Type</th>
<th>Sample Codes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry Toner DP</td>
<td>Uncoated</td>
<td>Stitched Hardcover</td>
<td>DT_Uncoated</td>
</tr>
<tr>
<td>Liquid Toner DP</td>
<td>Uncoated</td>
<td>Stitched Hardcover</td>
<td>LT_Uncoated</td>
</tr>
<tr>
<td>Offset Lithography</td>
<td>Uncoated</td>
<td>Stitched Hardcover</td>
<td>Offset_Uncoated</td>
</tr>
<tr>
<td>Dry Toner DP</td>
<td>Glossy</td>
<td>Glued Softcover</td>
<td>DT_Glossy</td>
</tr>
<tr>
<td>Liquid Toner DP</td>
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<td>Offset_Glossy</td>
</tr>
<tr>
<td>Dry Toner DP</td>
<td>Glossy w/30% Recycled</td>
<td>Stapled</td>
<td>DT_Glossy (Rec)</td>
</tr>
<tr>
<td>Liquid Toner DP</td>
<td>Glossy w/30% Recycled</td>
<td>Stapled</td>
<td>LT_Glossy (Rec)</td>
</tr>
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<td>Offset Lithography</td>
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<td>Stapled</td>
<td>Offset_Glossy (Rec)</td>
</tr>
<tr>
<td>Pigment Inkjet DP</td>
<td>Inkjet Glossy</td>
<td>Stapled</td>
<td>Inkjet_Glossy</td>
</tr>
</tbody>
</table>

for two weeks in a climate-controlled room at 21°C and 50% RH before testing.

**Chambers and Exposure Times**

The O₃ and NO₂ chambers were custom built by IPI by Codori Enterprises. The O₃ was produced by means of an ultraviolet lamp. The NO₂ chamber used tanks of 2% NO₂ purchased from Air Products. The temperature and humidity within chambers were held constant at 25°C ± 2°C and 50% RH ± 5% RH.

The bound and unbound materials placed in the O₃ chamber were exposed to 1 ppm O₃ for six weeks and those placed in the NO₂ chamber were exposed to 5 ppm NO₂ for six weeks. These conditions were selected because these were chamber conditions already in use for testing samples for a different experiment.

**Sample Arrangements in the Chambers**

The bound materials were placed independently in the NO₂ and O₃ chambers as follows. The hardcover and glued softcover books printed using three different presses were placed vertically next to each other, as they would be found on library shelves (Figure 2a). The stapled periodicals printed using four different presses were laid flat as one might find them in a library's magazine section (Figure 2b). In addition, the unbound sheets were hung freely in the pollution chambers on a rod with 2 cm gaps between the samples (Figure 2c).

**Results**

**Unbound Free-Hanging Samples**

Figure 3 shows the ΔE*ₜₐᵢₜ of a white patch after the O₃ exposure for all papers tested. Visually, yellowing of the papers was not observed after O₃ exposure, and the data only showed a small change in ΔE*ₜₐᵢₜ.

Figure 4 shows the ΔE*ₜₐᵢₜ of a white patch after the NO₂ exposure. Glossy and glossy paper with 30% recycled content showed the greatest increase in ΔE*ₜₐᵢₜ. Visually, NO₂ exposure caused yellowing of all substrates except for the inkjet glossy paper, for which there was no noticeable change.

O₃ exposure had a greater impact on colorant fade than NO₂ exposure. Figure 5 shows the ΔE*ₜₐᵢₜ of white and Dmax CMYK patches after O₃ exposure. The liquid-toner digital press showed the largest cyan and magenta colorant fade regardless of the paper on which it was printed. The inkjet digital press had the highest ΔE*ₜₐᵢₜ of 13.8 for the cyan patch. Dry toner EP and offset press samples had ΔE*ₜₐᵢₜ color differences below 3.1 for all colorants.

Figure 6 shows ΔE*ₜₐᵢₜ color differences for Dmax CMYK patches after NO₂ exposure. A white patch was also included.
as a guide to determine whether paper yellowing influenced colorant change. The cyan and white patches had the highest ΔE⁰ values for the cyan patch. Examination of the data revealed a similar magnitude and direction of change in the CIELAB color space between paper white and the cyan patch, suggesting that the cyan colorant change was most likely due to the yellowing of the substrate and not the loss of cyan colorant. However, paper yellowing did not seem to have as big of an effect on the yellow, magenta, and black colorants. The black patch, on the other hand, did not reflect or transmit much light at all, and thus its color was minimally affected by the paper yellowing.

Bound Materials

There was a very small change in the yellowing of the substrates after O₃ exposure in bound materials and free-hanging samples. Therefore, the O₃ data from the bound materials for paper yellowing was omitted from this paper. Likewise, the colorant data after the NO₂ exposure showed confounding ΔE⁰ results in bound materials due to the substrate yellowing. Thus, the NO₂ data for color patches from bound materials was omitted.

Overall, the bound materials did not show the same degree of yellowing throughout the pages as the free-hanging samples after the NO₂ exposure. While the book cover or the text block as a whole might have protected the center of the pages from pollutant penetration, yellowing was still observed on the edges and in the gutter. Figure 7 shows ΔE⁰ values for the white patch after NO₂ exposure. The bar graph plots data read from the center of the book against data from the middle of the gutter and the edges of the pages. All of the bound materials had ΔE⁰ values greater than 1.0 for the paper edges. However, stapled periodicals had the largest ΔE⁰ values for all page sections (center, gutter, and edges). The larger gaps between pages in the stapled periodical, a result of the pages being less densely packed together, allowed NO₂ to penetrate easily (see Figure 8). Although the hardcover book shielded the center and the middle of the gutter from yellowing, the edges were still affected. The softcover book showed yellowing in the middle of the gutter and at the edges, but not in the center.

One of the stapled periodical samples from the graph in Figure 7, Liquid-Toner Glossy (Rec), is shown in Figure 9 below. Yellowing was severe at the page edges and gutter. The center of the page did not show as much yellowing as the other sections. Additionally, this example shows the yellowing effect in the middle pages of the book, which had a gap when closed due to the stapled binding, allowing for pollutant penetration. In Figure 8, the image was manipulated in Adobe Photoshop using the Hue/Saturation tool to improve reproduction of yellowing of the page edges and the gutter resulting from NO₂ exposure in both B&W and color publications. Dark areas illustrate where the yellowing has occurred.

The colorant fade in bound materials after O₃ exposure was not as dramatic as in the free-hanging samples. However, the sta-
Conclusions

The study showed that bound digitally-printed and unbound materials were affected by the exposure to O$_3$ and NO$_2$. Exposure to O$_3$ contributed more to the fading of the colorants, while exposure to NO$_2$ contributed to substrate yellowing. This research revealed that the free-hanging samples yellowed across the entire surface as a result of NO$_2$ exposure while the bound materials only exhibited yellowing on the edges. In general, the page centers were shielded by the hardcover and softcover bindings. However, the stapled periodical showed yellowing in the page centers and in the middle of the gutter due to the large gaps between the pages allowing for greater NO$_2$ penetration. It was also noted that the cyan patch exhibited colorant change after NO$_2$ exposure, which was more likely due to the substrate yellowing than cyan colorant loss. With regard to the O$_3$ exposure of the free-hanging samples, the liquid-toner EP and inkjet press samples showed the greatest cyan and magenta fade regardless of the paper it was printed on. However, the bindings mitigated O$_3$ penetration inside the books and reduced colorant degradation, except for the stapled inkjet periodical, which showed cyan and magenta colorant fade. There is still more research needed to be done on this matter. In this experiment, binding types were only paired with a specific paper. In future work, a wider selection of papers with different bindings, pollutant concentrations, page numbers, and different sample arrangements should be considered.

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References


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Nino Gordeladze, Research Associate, has been working for the Image Permanence Institute since 2008. She graduated from Rochester Institute of Technology with a Bachelor of Science in Imaging and Photographic Technology in 2010. She also received an Associate degree in Business Administration from Hudson Valley Community College in 2007. Currently she is working on the DP3 (digital print preservation portal) research projects funded by IMLS and the A. W. Melton Foundation. Some of her work includes investigating the stability of digital prints in bound forms, the pollution-mitigations strategies, and thermal stability of the digital print colorants.