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# Yellowing of Digitally Printed Materials in Cultural Heritage Collections

## ABSTRACT

The purpose of this project was to quantify the effects of temperature and humidity on the yellowing rates of digital prints in cultural heritage collections. Heat and humidity are the only two material stresses that can't be eliminated from storage and therefore ultimately determine the maximum limit of how long a digitally printed object can last. Heat is damaging by itself, but it also amplifies other chemically driven decay forces. The thermal and humidity decay rates of many library and archive objects have already been studied, but no comprehensive study has been done to determine these rates for modern digitally printed materials. Understanding the thermal decay rates of materials can lead to the development of storage conditions that will ensure the object's accessibility and usability for extended periods. The Arrhenius method was applied to a large variety of papers used in digital printing (including inkjet, dye sublimation, and electrophotography) at three different humidities with incubations periods up to ninety-four weeks. It was found that the yellowing rates are highly dependent on both temperature and humidity and that digitally printed photographs were more prone to yellowing than digitally printed documents or prints made on digital presses. The yellowing differences among individual samples within a category were sometimes greater than between categories meaning that the prime determinant of a given print's stability may be the specific products (brands of colorants and paper) from which it was made rather than its category (e.g. inkjet photo paper). However, because most of the materials tested were predicted to last several centuries before noticeable yellowing at room conditions, the cost of reducing temperature or humidity to prevent yellowing may not be warranted.

## INTRODUCTION

Yellowing of digital print papers has been show to be caused by a variety of deterioration forces including heat, humidity, pollution, light, and enclosures. The purpose of this project was to quantify the effects of temperature and humidity on the yellowing rates of digital prints in cultural heritage collections. Heat and humidity are the only two material stresses that can't be eliminated from storage and therefore ultimately determine the maximum limit of how long a digitally printed object can last. The damage can be done to the paper substrates, surface coatings, or optical brightening agents.

Because all prints, whether on display or stored in the dark, are continually undergoing degradation due to heat and humidity, the first step in determining a strategy for their long-term care is usually to assess their thermal stability (natural aging rate) at a variety of potential storage humidities. Heat is damaging by itself, but it also amplifies other chemically driven decay forces. The thermal and humidity decay rates of many library and archive objects have already been studied, but no comprehensive study has been done to determine these rates for modern digitally printed materials. Understanding the thermal decay rates of materials can lead to the development of storage conditions that will ensure the object's accessibility and usability for extended periods.

The quantity of digitally printed materials in collections is enormous and continues to grow. A 2008 survey of libraries, museums, and archives found that 87% of institutions already have digital prints and that 30% of them have seen yellowing of some portion of their digital print collections.[1] Because digital prints are a relatively new type of collection asset this is clearly a serious problem. This project focused only on the thermal yellowing of prints and did not study other forms of thermal damage such as colorant deterioration (e.g. fade or bleed) or physical deterioration of the substrate (e.g. embrittlement or delamination). This study was part of a larger project intended to evaluate the effects of a wide variety of deterioration forces on modern digital prints. Results of IPI's other studies on the stability of digitally printed

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materials in cultural heritage collections can be found at www.DP3Project.org.

Below are descriptions of the three major digital printing technologies that were studied in this project:

- *Inkjet*—This technology is used by many home and office desktop printers. Small droplets of ink in an aqueous solution are rapidly jetted onto the printing paper. In addition to the desktop printers, there are also some wide-format inkjet printers that are typically used to create large images for fine art or commercial purposes. Inkjet printing is used for both documents and images.
- *Dye Sublimation*—In these systems, the image-forming colorants are transferred to the print paper from colored donor ribbon. The printer modulates heat energy to the colored ribbons to control the amounts of yellow, magenta, and cyan dyes that are transferred. This technology is most often used in consumer snapshot-size photo printers and in commercial photo kiosks. This process is only used to created pictorial images. It is never used to create documents.
- *Color Electrophotography*—This process is mostly used to produce documents from laser printers. In color electrophotographic systems, color toners are deposited on the printing paper by an electrical charge (modulated by a laser or LED array) and "fixed" by heat or pressure. The toners are usually pigments with the black toner being very stable carbon black. Electrophotography is also the primary technology used in production digital presses where digital printing technology has been scaled up from the desktop and office size printers to devices that print hundreds to thousands of copies for short-run periodicals and monographs.

The experiment also included traditional print materials whose behaviors (at least in general, if not in these specific experimental conditions) are already known. Direct comparison with these older and more familiar print materials should provide important context for the results of this project. Three types of printing papers were used as comparison controls in the experiments: traditional silver-halide color photographic paper, standard office paper used in black-and-white electrophotographic printing, and offset lithographic papers.

## METHOD

The method most commonly used to evaluate the temperature dependence of a material is the Arrhenius Method, named for the Swedish chemist Svante Arrhenius. This method forms the basis of the ISO standard 18924 *Imaging materials—Test Method for Arrhenius-type Predictions* developed to evaluate the thermal stability of imaging materials in particular. The Arrhenius method is a mathematical treatment of data that allows for predicting the stability of materials at a reduced temperature (such as room conditions) from accelerated aging tests. IPI has successfully used this approach in the past to determine the deterioration rates for photographic film bases and traditional color photographic dyes. This complex technique requires incubating the printed materials at a series of temperatures for increasing periods of time. The logarithm of time to failure (noticeable yellowing) of the print is graphed against reciprocal temperature in Kelvin, and the resulting line is extrapolated to predict time to failure at room temperature (or any other temperature such as cold storage). Performing the test at various humidities can give institutions an estimate of how the collection materials will perform over time at a variety of possible temperature and humidity combinations.

For this experiment, an increase in status A blue density of 0.05 was used as the failure point. This was chosen because it is clearly noticeable yellowing and because higher levels would extend the test periods beyond the project's three-year limit. This level of yellowing may or may not be the level of change considered objectionable for all uses and by all institutions; however, some level needed to be selected and the use of the same level for all extrapolations would allow for comparisons between the different temperature and humidity combinations. The 0.05 level is in no way to be considered the level at which the print will be unusable or unreadable.

Because the goal of the project was to determine the thermal stability of collections of digital prints as opposed to specific digital print products, a large number of different digital print types with multiple representations of each would be necessary to create a realistic surrogate test population. For these experiments, a total of 28 different printing paper types that covered the entire range of the major digital printing technologies and their more common sub-categories were included. The materials tested and their primary end uses (photographs, documents, and production printing) are listed in tables 1–3.

The individual papers were then grouped into categories that collection care personal could be trained to differentiate (they would not be able to identify prints to the level of specific products). These categories would be used to report the results. These categories are listed in tables 4–6.

The papers were all unprinted except the color silver halide paper which was unexposed and processed to paper white and the dye sublimation paper which was printed with no image so that the clear overcoat used in the system would be applied. All papers were tested in triplicate. The samples were measured with a GretagMacbeth Spectrolino for Status A blue density. The device conformed to ISO 5–3: 2009 *Photography and graphic technology—Density measurements—Part 3: Spectral conditions* and ISO 5–4: 2009 *Photography and graphic technology—Density measurements—Part 4: Geometric conditions for reflection density*. It was assumed that since none of the samples were printed with an image that all samples for each

| *Printing Technology* | *Paper* |
|---|---|
| Inkjet | Porous-coated photo |
| Inkjet | Porous-coated photo |
| Inkjet | Polymer-coated photo |
| Inkjet | Polymer-coated photo |
| Inkjet | Inkjet-sized plain |
| Inkjet | Porous-coated plain |
| Inkjet | Inkjet-sized fine art |
| Inkjet | Porous fine art |
| Inkjet | Porous fiber-base fine art |
| Inkjet | Porous fiber-base (warm tone) |
| Dye sublimation | Dye sublimation paper |
| Dye sublimation | Dye sublimation paper |
| Dye sublimation | Dye sublimation paper |
| Color silver-halide | Chromogenic |
| Color silver-halide | Chromogenic |

Table 1. Photo Paper Test Samples

| *Printing Technology* | *Paper* |
|---|---|
| Inkjet | Inkjet-treated office paper |
| Inkjet | Inkjet-sized office paper |
| Electrophotography | Laser-specific office paper |
| Electrophotography | Color laser-specific office paper |
| Electrophotography | Virgin-pulp office paper |
| Electrophotography | 50% recycled-pulp office paper |
| Electrophotography | 100% recycled-pulp office paper |

Table 2. Document Paper Test Samples

| *Printing Technology* | *Paper* |
|---|---|
| Digital Press paper | Coated glossy |
| Digital Press paper | Coated matte |
| Digital Press paper | Uncoated |
| Offset lithography paper | Coated glossy |
| Offset lithography paper | Coated matte |
| Offset lithography paper | Uncoated |

Table 3. Production Printing Paper Test Samples

| *Printing Technology* |
|---|
| Inkjet |
| Dye sublimation |
| Color silver-halide |

Table 4. Photo Categories

| *Printing Technology* |
|---|
| Inkjet |
| Electrophotography |

Table 5. Document Categories

| *Printing Technology* |
|---|
| Digital press paper |
| Offset lithography paper |

Table 6. Production Printing Categories

paper would be acceptably similar to each other and that initial readings on every one of the over 12,000 samples included in this test would be unnecessary; however, every sample was measured after each incubation period for every temperature and humidity combination.

The samples were pre-conditioned at 21°C at each of three humidities (20%, 50%, and 80% RH) for one week. The samples were then placed into aluminum foil-laminate bags, the air was squeezed out, and the bags hermetically sealed. The samples were incubated in foil bags to ensure constant moisture content of the samples throughout the experiment as well as protect them from atmospheric pollutants. All of the bags required for a single incubation period at each temperature and humidity were then put into another bag, the air was squeezed out and the outer bag was hermetically sealed. The double bag provided assurance that the moisture contents wouldn't change due to possible pin holes through the metal foil layer in the inner bags.

For this study, IPI used 55°C, 65°C, 75°C, and 85°C as the series of temperatures and 20%, 50% and 80% as the various potential storage humidities to evaluate. The time periods ranged from one week to nearly two years depending on the temperature. Higher temperatures needed shorter incubation periods and lower temperatures needed longer test periods. Enough samples for twelve different incubation periods for each temperature and humidity combination were prepared. Twelve pull times, with three moisture contents, incubated at each of four temperatures in triplicate required 432 specimens for each product. This made for over 12,000 samples for the entire experiment. Because the thermal rates of the materials are not known in advance it is impossible to know how long the incubation periods need to be. Estimations based on experience with previous materials were helpful but adjustments to the initial time estimates would need to be made as the experiment progressed.

From the data, years to endpoint would be predicted at 10ºC, 20ºC, 30ºC at 50% RH to compare the effects of temperature on print yellowing. In addition, years to endpoint would also be predicted for 21ºC at 20%, 50%, and 80% to compare the impact of humidity on yellowing. It should be noted that as long as samples at two temperatures reach endpoint for any humidity level, it would be possible to make an Arrhenius prediction, however, with only two data points, the quality of the prediction could potentially be very low.

After approximately six months of incubation, the data collected to date was extrapolated to create rough predictions of the incubation periods that would subsequently be required to reach the 0.05 status A blue density increase for the samples that had not yet reached endpoint. These first predictions indicated that it would require over seven years for some samples to reach endpoint using the current test temperature and humidity conditions. This was significantly longer that originally anticipated. For this reason the remaining incubation periods were extended to more closely match these first rough calculations of required incubation times. Additional samples were also created and added to the experiment at two intermediate temperatures: 70°C and 80°C. These would reduce the overall time for the experiment to be completed as a greater number of samples would reach endpoint before the end of the project.

## RESULTS

The samples were incubated for one to ninety-four weeks. Not all of the samples reached the yellowing endpoint for all six temperatures during this period. A significantly larger number of samples reached endpoint at the high temperatures and elevated humidities than at low temperatures and low humidity. The predictions below are based on the largest number of temperature values possible for each humidity, but could be as low as just two.

Figures 1–3 below illustrate the effects of temperature on years to noticeable yellowing for the various categories of digitally printed materials: photographs, documents, and production printing. The range of values for the various individual samples within each category is represented by the black lines within each bar.

Figures 4–6 below show the effects of humidity on years to noticeable yellowing for the various categories of digitally printed materials: photographs, documents, and production printing. The range of values for the various individual samples within each category is represented by the black lines within each bar.

Digitally printed photographs were more prone to thermal-induced yellowing than digitally printed documents or prints made on digital presses. Of all the photograph paper categories, dye sublimation prints were the most sensitive to yellowing. The worst paper tested was an inkjet fine-art paper, though that paper is not common and may be rarely found in collections. Temperature and humidity variations clearly had a significant effect on the yellowing rates of all the print types. However, because most of the materials tested should last several centuries before noticeable yellowing, the cost of reduced temperature below human comfort levels or humidity levels below 50% to prevent yellowing may not be warranted.

The bars showing the range of individual sample performances were extremely wide. In some cases the samples within a category varied more than the categories themselves. This means that the prime determinant of a given print's stability may be the specific products (brands of colorants and paper) from which it was made rather than any class or category it can be ascribed to. The strategies to preserve collections of digital prints should still be made for each of the different print categories and sub-categories, but collection care staff will have to pay attention to their collections to watch out for individual

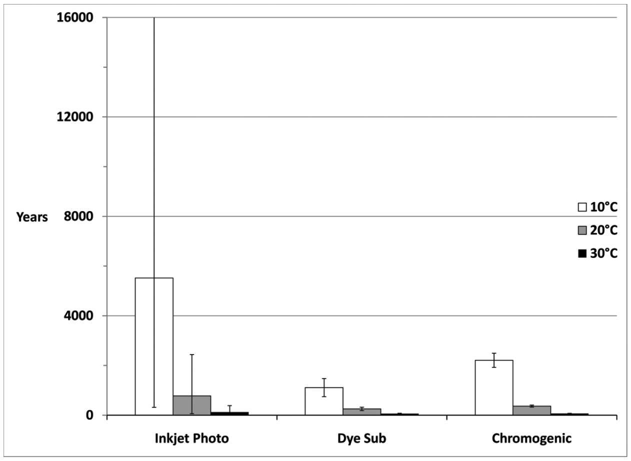

Fig. 1. Predicted Years to Just Noticeable Yellowing of Digitally Printed Photographs at 50% RH

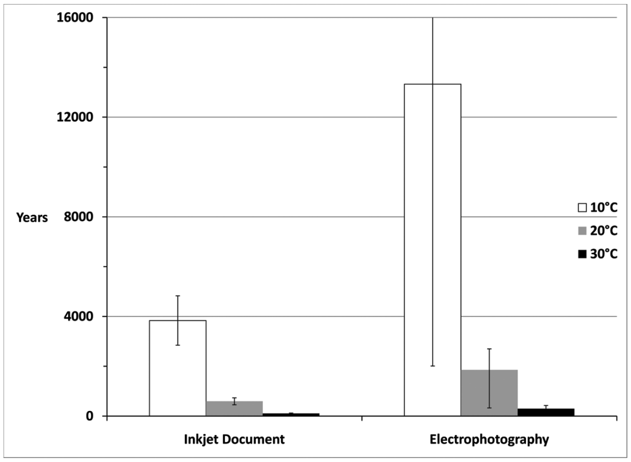

Fig. 2. Predicted Years to Just Noticeable Yellowing of Digitally Printed Documents at 50% RH

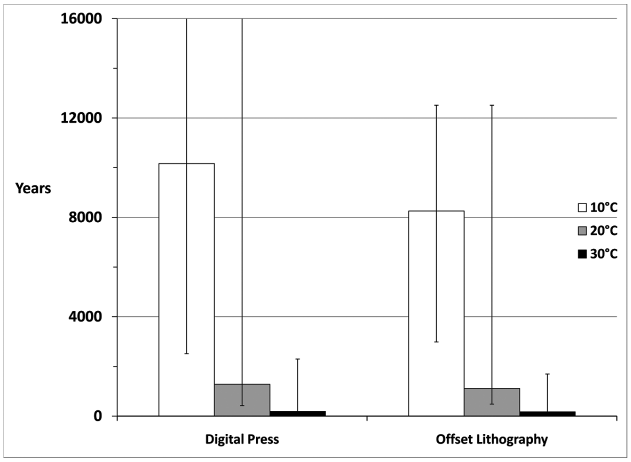

Fig. 3. Predicted Years to Just Noticeable Yellowing of Digital Production Prints at 50% RH

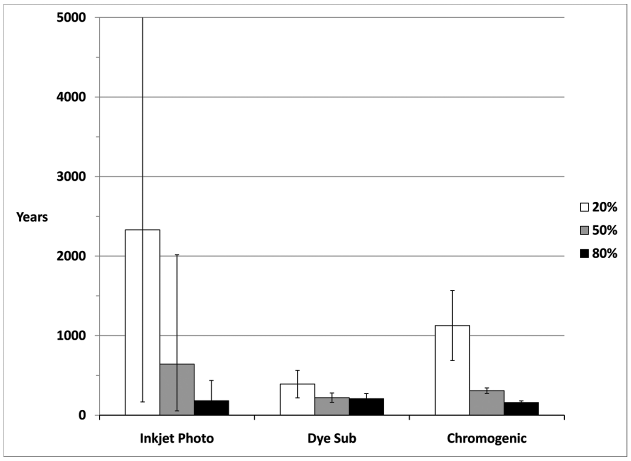

Fig. 4. Predicted Years to Just Noticeable Yellowing of Digitally Printed Photographs at 21°C

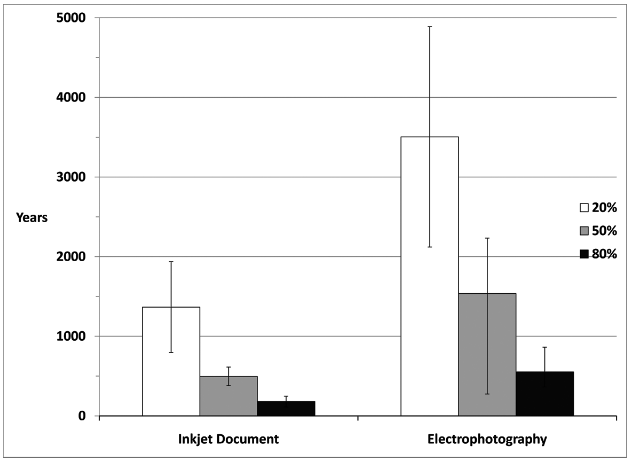

Fig. 5. Predicted Years to Just Noticeable Yellowing of Digitally Printed Documents at 21°C

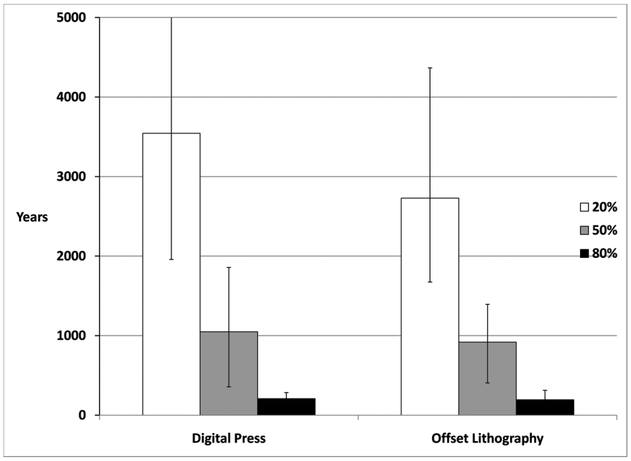

Fig. 6. Predicted Years to Just Noticeable Yellowing of Digital Production Prints at 21°C

prints that may differ from the trends of their category and experience an even greater rate of decay.

The data also suggested that the yellowing reported in the 2008 survey by institutions is probably not from thermal-induced decay but from one of the other factors such as light or air pollutants. Digital printing has been around for only three decades, and most collection materials will come from the latter part of that period. Because the weakest material under room conditions should last 64 years before noticeable yellowing, it is unlikely that natural aging is the cause of the damage these institutions have reported. Efforts to prevent yellowing should not focus on reduced temperature or humidity but on reduced exposure to light and open air.

## CONCLUSIONS

The following conclusions were drawn from the data:

- Digitally printed photographs were more prone to yellowing than digitally printed documents or prints made on digital presses.
- The yellowing rates are highly dependent on both temperature and humidity.
- The yellowing differences between individual samples were sometimes greater than between categories. This means that the prime determinant of a given print's stability may be the specific products (brands of colorants and paper) from which it was made rather than its category (e.g. inkjet photo paper).
- Because most of the materials tested should last several centuries before noticeable yellowing at room conditions, the cost of reducing temperature below human comfort levels or humidity below 50% to prevent yellowing may not be warranted.
- Because yellowing is likely not the only important form of deterioration influenced by temperature, storage temperature and humidity recommendations cannot be made based solely on yellowing rates.

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## NOTE

1. Burge, D., D. Nishimura, and M. Estrada 2009. Summary of the DP3 Project Survey of Digital Print Experience within Libraries, Archives, and Museums. In *Final Program and Proceedings, Archiving 2009, May 4–7, 2009, Arlington, VA*. Springfield, VA: Society for Imaging Science and Technology. 133–136.

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