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Reanalysis of Yellowing of Digitally Printed Materials in Cultural Heritage Collections

ABSTRACT

This paper is a retraction and re-analysis of data presented previously (Nishimura et al. 2011). As it turned out, the program running the GretagMacbeth spectrolino/spectroscan outputs the data in a different order depending on which device the reading head is attached to. This error was not obvious either during measurement or analysis and was discovered quite by accident. For further details about the original work, please refer to *Book and Paper Group Annual* 30.

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 objects' 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 incubation periods of up to 94 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).

INTRODUCTION

Digital print papers are known to yellow from a variety of deterioration forces including pollution (Burge et al. 2010, Burge et al. 2011), light (Venosa et al. 2011), and enclosures (Burge and Rima 2010). The purpose of this project was to quantify the effects of heat and humidity on the yellowing rates of digital prints in cultural heritage collections, as these are the only two stress factors that can't be removed from the storage environment. Prints can be stored in opaque boxes or in dark storage rooms to prevent light damage. The air within storage and display areas can be filtered to prevent pollution damage. Proper enclosures can also be selected, but there will always be some level of heat and humidity. Thus, heat and humidity are factors that ultimately determine the maximum limit of how long a digital print will last. The thermal and humidity decay rates of many library and archive objects have already been studied (Browning and Wink 1968, Adelstein et al. 1970, Brown et al. 1983, Adelstein et al. 1992, Nishimura 1992, Van Bogard 1995), but no comprehensive research has been done to determine these rates for modern digitally printed materials. Understanding the thermal decay rates of materials will aid in the development of appropriate storage environment standards that can ensure the long-term accessibility and usability of these objects.

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 30% of them have seen yellowing of some portion of their digital print collections (Burge et al. 2009). Below are descriptions of the major digital printing technologies that were studied in this project:

- *Inkjet* – This technology, in which small drops of liquid ink are rapidly jetted onto the printing paper, is used in many home and office desktop printers. It is also used in

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Table 1. Photo Papers

Printing Technology	Paper Type	No. of Examples
Inkjet	Porous-coated photo	2
Inkjet	Polymer-coated photo	2
Inkjet	Porous-coated plain	3
Inkjet	Porous fine art	3
Dye sublimation	Dye sublimation paper	1
Color silver halide	Chromogenic	2

Table 2. Document Papers

Printing Technology	Paper Type	No. of Examples
Inkjet	Inkjet-treated office paper	1
Inkjet	Inkjet-sized office paper	1
Electrophotography	Laser-specific office paper	1
Electrophotography	Color laser-specific office paper	1
Inkjet/Electrophotography	Virgin-pulp office paper	1
Inkjet/Electrophotography	50% recycled-pulp office paper	1
Inkjet/Electrophotography	100% recycled-pulp office paper	1

Table 3. Press Papers

Printing Technology	Paper Type	No. of Examples
Digital Press paper	Coated glossy	1
Digital Press paper	Coated matte	1
Digital Press paper	Uncoated	1
Offset lithography paper	Coated glossy	1
Offset lithography paper	Coated matte	1
Offset lithography paper	Uncoated	1

wide-format printers to produce fine art and commercial signage. Production digital presses are just starting to use this technology.

- *Dye Sublimation* – This system, in which the image-forming colorants are transferred by heat to the printing paper from a donor ribbon, is only used for printing images – never documents.
- *Color Electrophotography* – This process, in which color toner particles are temporarily held on to the printing paper by an electrostatic charge before being "fixed" to the paper by pressure, heat, or both, is primarily used to produce documents, although it is also used for large-scale commercial digital presses.

This project also included traditional print materials as benchmarks. Direct comparison with these older and more familiar print materials should provide an important context for the results of this project. Two types of printing papers were used as comparison controls in the experiment: traditional silver-halide color photographic paper and offset lithographic paper.

METHOD

The Arrhenius Method (ISO 2013) was used to create predictions based on test results from high temperature incubations. In this method, replicate samples were incubated at six temperatures and three humidities (18 total conditions) to determine approximately how long it might take them to yellow at room condition and to determine their sensitivity to humidity and temperature.

Since this project dealt only with the substrates and not the colorants, non-imaged substrate samples were used. Currently, a separate study is underway to examine the thermal fading of colorants. For this yellowing project, an increase in Status A blue density[1] of 0.05 was used as the endpoint, representing a clearly noticeable level of yellowing without requiring incubation times beyond the end of the project. However, this level does not represent the point at which the print is no longer readable or usable.

Because the goal of the project was to determine the thermal stability of collections of digital prints rather than specific digital print products, a large number of different digital print types with multiple representations of each were required to create a realistic surrogate test population. A total of 28 different printing papers were used to cover the range of the

Table 4. Photo Categories

Printing Technology
Inkjet
Dye sublimation
Color silver halide

Table 5. Document Categories

Printing Technology
Inkjet
Electrophotography

Table 6. Press Categories

Printing Technology
Digital press
Offset lithography

major digital printing technologies and their common subcategories. The materials tested and their primary end uses are listed in tables 1–3.

The individual papers were then grouped into categories that collection-care personnel could be trained to differentiate, and these categories were used to report the results. These categories are listed in tables 4–6.

The papers were all unprinted except the color silver-halide photographic 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. This 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, all samples for each paper would be similar enough to one another that initial readings on each of the more than 12,000 samples included in this test would not be necessary. Instead, a representative group of 30 samples from each paper was measured and averaged, with the average representing the initial value for each paper. However, all samples were measured after each incubation period for every temperature and humidity combination.

Six temperatures were used for the accelerated aging: 55°C, 65°C, 70°C, 75°C, 80°C, and 85°C. The moisture content of the samples was held constant by conditioning the samples to 21°C and 20% RH, 50% RH, or 80% RH for one week and then sealing the samples in foil bags. Samples were incubated at various intervals depending on temperature up to 94 weeks until the 0.05 endpoint was reached. Using the standardized Arrhenius prediction methodology, the logarithm of the incubation times to reach 0.05 D_{min} gain for each temperature was then plotted against the reciprocal of the absolute test temperatures, and the predicted time to reach 0.05 D_{min} gain at 10 °C, 20 °C, and 30 °C extrapolated. While any range of temperatures could show the relative effects of temperature on the yellowing of digital print substrates, this particular range was chosen to cover a common range of temperatures one might find in typical collections from cool to fairly uncontrolled conditions. In addition, years to endpoint would also be predicted for 21°C at 20% RH, 50% RH, and 80% RH to compare the impact of humidity on yellowing.

RESULTS

Tables 7–9 illustrate the effects of temperature on predicted years to noticeable yellowing for the various categories of digitally printed materials: photographs, documents, and production press printing. The worst and best case samples in each category are reported along with the average for the category.

Tables 10–12 show the effects of humidity on predicted years to noticeable yellowing for the various categories of digitally printed materials: photographs, documents, and production printing.

Inkjet prints were the most prone to yellowing of the digital technologies, followed by electrophotography and dye sublimation. Digital photographs were more prone to yellowing than digitally printed documents.

Statistical tests on the data across the range of 20 Celsius degrees for temperature and across 60 percentage points for relative humidity showed that temperature had the most significant effect on the time to noticeable yellowing, followed by RH. However, a drop in humidity from 50% to 20% did have a profound effect on extending the life of the worst case samples. There is also a significant synergistic effect of temperature and RH, so the largest benefit would be obtained by reducing both temperature and RH. This benefit is greater than can be accounted for by simply adding the effects of changing temperature alone and humidity alone. Note that the RH data for the dye sublimation and chromogenic papers were somewhat erratic. The reason for this is not known.

The values in tables 10–12 indicate an extreme range of responses for the materials, from 1 to nearly 15,000 years. Low values such as a single year will be highly alarming to collection caretakers, while 15,000 years is probably far beyond their concerns. It may be helpful to think in terms of percentages within each category that may reach the reasonable preservation goals of 50 or 100 years. Table 13 shows the percentage of materials within each category expected to yellow by 50 and 100 years. Inkjet was the most prone to yellowing by 50 years, though the number that yellowed by 100 years was not much higher, indicating that yellowing may appear quickly and then slow down with additional time. At

Table 7. Effect of Temperature on Digitally Printed Photos (in Years)

		Worst case	Average	Best case
Inkjet Photo	10 °C	7	1515	5054
	20 °C	3	222	673
	30 °C	1	37	102
Dye Sublimation	10 °C	715	2570	4454
	20 °C	165	502	892
	30 °C	42	110	199
Chromogenic	10 °C	3	7477	14950
	20 °C	2	783	1564
	30 °C	1	95	190

Table 8. Effect of Temperature on Digitally Printed Document (in Years)

		Worst case	Average	Best case
Inkjet Document	10 °C	49	3898	8017
	20 °C	12	530	1045
	30 °C	3	83	156
Electrophotography	10 °C	568	3770	8017
	20 °C	100	515	1045
	30 °C	19	81	156

Table 9. Effect of Temperature on Digital Press Prints (in Years)

		Worst case	Average	Best case
Digital Press	10 °C	305	1255	2946
	20 °C	56	193	425
	30 °C	11	34	70
Offset Lithography	10 °C	310	1470	3222
	20 °C	59	216	448
	30 °C	13	36	71

100 years, the electrophotographic samples caught up with the inkjet. The dye sublimation prints were highly resistant to thermal yellowing.

Given the large number of papers available on the market (and over the history of digital printing), for most of the printing technologies, the sample set was unfortunately small out of necessity.[2] However, assuming that the sample sets were, in fact, fairly representative of the population, room-condition storage of these materials can be expected to result in significant, widespread yellowing at 100 years.

ACTIVATION ENERGY

Activation energy is the energy necessary to initiate a reaction and provides a measure of the temperature dependence of the reaction rate. It therefore provides an idea of how much benefit colder storage will have and, conversely, how bad warmer storage will be. Table 14 ranks the materials based on their activation energy from low to high. Acetate film base is included as a reference because many collection-care personnel are familiar with its behavior.

The vast majority of digital printing papers had fairly high activation energies. This is both a blessing and a curse. On the positive side, just dropping the storage temperature by a few degrees can greatly improve the time to yellowing for these materials. On the negative side, papers in poor storage conditions are in very serious trouble.

Importantly, the range of individual sample performances within categories was quite wide, such that samples within a category often varied more than the categories themselves. Unfortunately, this means that stability may not be so much a function of paper type, but rather of the specific product (brand of paper) from which the print was made. Strategies for preserving collections of digital prints should still be made for each of the different print categories and sub-categories, but collections care staff must be aware that there may be prints that differ from general category trends. The data also suggested that at least some of the yellowing reported by institutions in the 2008 survey may be thermally induced, though it may have been made worse by exposure to atmospheric pollutants.

Table 10. Effect of Humidity on Digitally Printed Photos (in Years)

		Worst case	Average	Best case
Inkjet Photo	20% RH	17	528	1804
	50% RH	2	185	555
	80% RH	2	60	159
Dye Sublimation	20% RH	165	284	403
	50% RH	143	429	764
	80% RH	162	426	899
Chromogenic	20% RH	39	280	521
	50% RH	1	630	1259
	80% RH	4	48	92

Table 11. Effect of Humidity on Digitally Printed Documents (in Years)

		Worst case	Average	Best case
Inkjet Document	20% RH	56	994	2056
	50% RH	11	438	859
	80% RH	5	185	343
Electrophotography	20% RH	194	1002	2056
	50% RH	84	425	859
	80% RH	81	191	343

Table 12. Effect of Humidity on Digital Press Prints (in Years)

		Worst case	Average	Best case
Digital Press	20% RH	112	292	580
	50% RH	48	161	353
	80% RH	9	73	134
Offset Lithography	20% RH	133	675	1585
	50% RH	50	180	371
	80% RH	14	80	142

Table 13. Percentage of Test Samples Yellowed After 50 and 100 Years at 21°C and 50% RH

Material	% Yellowed by 50 years	% Yellowed by 100 years
Inkjet photo	40%	56%
Dye sublimation	0%	0%
Inkjet document	20%	20%
Electrophotography	0%	20%
Digital press	0%	67%

Table 14. Activation Energies (in kJ mol^{-1} K^{-1})

Material	Activation energy
Acetate film base	88
Chromogenic	106
Dye sub	111
Inkjet photo	119
Digital press	122
Offset lithography	126
Inkjet document	129
Electrophotography	131

CONCLUSIONS

The following conclusions were drawn from the data:

- Digitally printed photographs are more prone to yellowing than digitally printed documents
- Inkjet was the most sensitive to yellowing, followed by electrophotography, while dye sublimation was highly resistant to thermal yellowing
- Yellowing rates are highly dependent on both temperature and humidity
- Yellowing rates were often more variable between individual products within a category than between categories

This project only dealt with yellowing of the printing paper. The physical integrity of the support and the stability of the colorants must also be considered. Final recommendations for storage conditions for these materials will need to wait until such additional research is completed. As mentioned earlier, work is currently underway at IPI to evaluate colorant stability.

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NOTES

1. Status A blue density is the base 10 logarithm of the reciprocal of the reflectance as measured through a blue filter with spectral properties and geometry as defined by 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***.** Reflectance is the fraction of the light received by the object that is reflected.

2. Given that six temperatures and three humidity conditions were used with a potential for 12 pull times, each additional paper would add 216 specimens to the project.

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