Light-Induced and Thermally-Induced Yellowish Stain Formation in Inkjet Prints and Traditional Chromogenic Color Photographs

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Abstract: Inkjet printing of photographs using both dye-based and pigmented inks has become the most popular form of hardcopy output from digital camera files. In addition to desktop and wide-format applications, inkjet printing technology is now also being adopted for "dry" minilabs and by professional portrait and wedding photography studios. Various factors affecting both light-induced and thermally-induced yellowish stain formation in inkjet prints are described. Stain behavior for representative inkjet papers as well as for selected traditional chromogenic color prints are discussed. Using data obtained from high-intensity 35 klux tests and with long-term 1.0 klux tests, potential stain formation and optical brightener activity loss reciprocity failures are described. Problems with the integration of light-induced and thermally-induced yellowing data in accelerated image stability tests are also discussed.

Introduction

Color photography has had a very long history of problems with gradual yellowish stain formation that has occurred both with prints stored in the dark and when exposed to light on long-term display. Kodacolor, introduced by Eastman Kodak in 1942, was the first mass market chromogenic color negative film and color print process and was the historical predecessor of today's chromogenic color film and print materials. With prints made for more than a decade after its introduction, Kodacolor prints suffered from severe thermally-induced yellowish stain that developed gradually during storage. Some examples studied by this author now have d-min blue densities of above 1.0.

These Kodacolor prints also had very poor light stability and, with no known examples of prints still surviving in reasonable condition, that period of color photography has been referred to as "The Totally Lost Kodacolor Era of 1942–1953." The primary cause of the yellowish stain that occurred in dark storage has been attributed to the presence of non-reacted magenta coupler remaining in the prints at the completion of processing and washing. Over time, these residual couplers can develop significant stain levels. Improvements were made by Kodak in 1954–55, but magenta coupler-produced-stain continued to be a problem for chromogenic prints. As shown in Figures 1 and 2, further complicating the matter is the fact that rates of yellowish stain formation may significantly increase when prints are stored in the dark after exposure to light during display.[1]

The first "low thermal stain" color negative paper was introduced by Fuji in 1985 under the Fujicolor Paper Type 12 name. Further improvements were made by both Fuji and Konica and in the early 1990's both companies introduced further improved products. Kodak's first "low thermal stain" color negative papers, Ektacolor Edge 7 and Portra III, were introduced in the mid-1990's.

With the advent of digital minilabs introduced in recent years by Fuji, Agfa, Konica, Noritsu, and other companies, chromogenic color papers such as Fujicolor Crystal Archive and Kodak Generations are now extensively used for printing digital camera files.

Inkjet Prints

Photographic-quality inkjet prints came into the market in the mid-1990's and now, with printers, inks, and media supplied by Epson, Hewlett-Packard, Canon, Lexmark, and others, the great majority of prints made by consumers from digital camera files are printed at home with inkjet printers. Desktop and large-format inkjet printers are also extensively used by professional and commercial photographers.

With inkjet printing, problems with yellowish stain have once again become a major area of concern. One of the key advantages of inkjet printing is the ability to print on a very wide variety of papers, films, canvas, and other substrates. Unfortunately, this wide choice of print media has resulted in products with a very wide range of quality. Some have poor yellowing behavior, either in dark storage, or when exposed to light on long-term display, or under both conditions. The introduction of high-stability pigmented and dye-based inksets by Epson, Hewlett-Packard, and others has further increased the stability demands on media.

Especially when inkjet prints are stored in albums or other dark locations, yellowish stain formation in the media – and not fading of the inks – may often be the limiting factor that determines the life of the prints.

Types of Yellowish Stain and Test Methods

There are a number of potential types and causes of yellowish stain formation in inkjet prints and in traditional

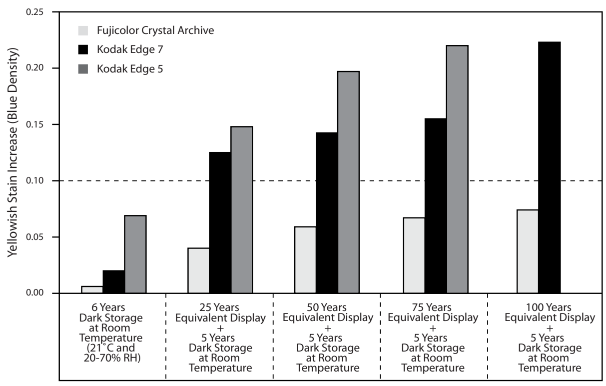

Figure 1. Light-induced "dark staining" with Fujicolor Crystal Archive Paper, Kodak Edge 7 Paper, and Kodak Edge 5 Paper. The three papers were exposed to the equivalent of 450 lux for 12 hours per day for the stated time periods before being placed in the dark for 5 years (100 year light exposure data for Edge 5 were not available). Nearly all of the yellowing occurred during the dark storage period.

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Table 1. WIR Visually-Weighted Endpoint Criteria Set v3.0 for Color Image Print Stability Tests

Ref. No.	Allowed Percentage of Change in Initial Status A Densities of 0.6 and 1.0[1]	Image Change Parameter
1	25%	Loss of cyan (red density) in neutral patches
2	20%	Loss of magenta (green density) in neutral patches
3	35%	Loss of yellow (blue density) in neutral patches
4	30%	Loss of cyan (red density) in pure color cyan patches
5	25%	Loss of magenta (green density) in pure color magenta patches
6	35%	Loss of yellow (blue density) in pure color yellow patches
7	12%	Cyan minus magenta (R – G) color imbalance in neutral patches
8	15%	Magenta minus cyan (G – R) color imbalance in neutral patches
9	18%	Cyan minus yellow (R – B) color imbalance in neutral patches
10	18%	Yellow minus cyan (B – R) color imbalance in neutral patches
11	18%	Magenta minus yellow (G – B) color imbalance in neutral patches
12	18%	Yellow minus magenta (B – G) color imbalance in neutral patches
Change Limits in Minimum-Density Areas (Paper White) Expressed in Density Units		
13	.06	Change [increase] in red or green density
14	.15	Change [increase] in blue density
15	.05	Color imbalance between red and green densities
16	.10	Color imbalance between red and blue densities
17	.10	Color imbalance between green and blue densities

[1]Initial (starting) densities are absolute measurements (not measured "above d-min"). A weighted criteria set for fading, color balance shifts, and d-min stain was first developed by H. Wilhelm in 1978–83 and was slightly modified in 1990, 1992, and 1996. Version 3.0 above was implemented on August 25, 2001 and for the first time included 0.6 starting densities for pure color cyan, magenta, and yellow in addition to the 1.0 starting densities for the pure color primaries that had been employed in earlier versions of the weighted criteria set. From the outset, the neutral scale parameters have always included both 0.6 and 1.0 starting densities.

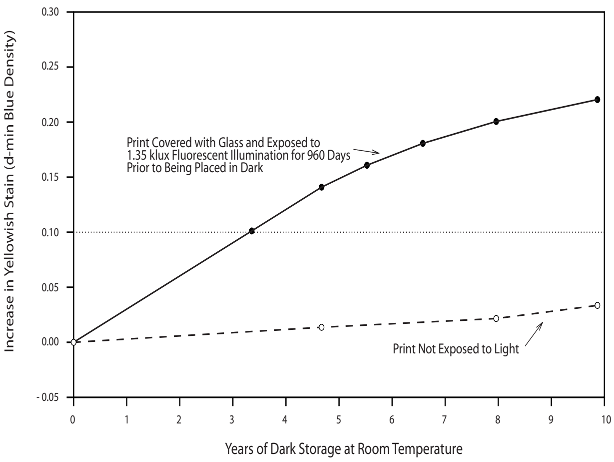

Figure 2. Light-induced "dark staining" of Ektacolor 74 RC Paper (initial type: 1977–82). Yellowish staining occurred at a much more rapid rate after a print was exposed to light for 960 days and then placed in the dark than it did in an identical print that was never exposed to light. Both prints were stored in the same environment.

color photographs; some such as light-induced and thermally-induced staining may affect both types of prints while others are specific to inkjet prints.

1) **Thermally-induced stain which occurs in dark storage.** Thermal stability is evaluated with the accelerated multi-temperature Arrhenius test which allows extrapolation of estimates to normal room temperature storage. The test procedure for traditional color photographic materials is described in ISO and ANSI standards.[2] It should be noted that the ANSI and ISO standards to date do not have an acceptability limit for d-min stain formation; only an illustrative endpoint of 0.06 d-min density color imbalance is given (or a d-min density increase of 0.10 if the 0.06 color imbalance is not exceeded). It is emphasized, however, that this endpoint is NOT a part of these standards. As listed in Table 1, Wilhelm Imaging Research has long used a d-min density color imbalance of 0.10 (or a 0.15 d-min density increase if the 0.10 d-min color imbalance is not exceeded, which is rarely the case).[3] Stain estimates for chromogenic papers have been published since the early 1990's by Fuji (most recently in an article Shibahara and colleagues[4)] and by Konica. Limited data have also been provided by Kodak.[5,6] Onishi of

Epson has applied the Arrhenius test method to a microporous inkjet paper printed with dye-based inks.[7] Wilhelm Imaging Research currently has Arrhenius tests in progress with a wide range of inkjet and other digital printing materials (see Figure 3). Additional data will be published in the future. The stain which occurs with inkjet prints, as well as with traditional color photographs, may occur in the imaging layer, in the paper or other support material, or in both. Research to date shows that the level of relative humidity can have a major impact on the yellowing of inkjet papers. These investigations also suggest that the "sealed vapor-proof bag" test method may not be applicable to testing inkjet prints and instead the "free-hanging" test method should be used. Thermally-induced stain itself may be relatively unstable on exposure to light (see Figure 4). Indeed, it appears possible that with high-stability pigmented inkjet inks printed on a media which has relatively poor thermal stability with respect to yellowing, the prints may take longer to reach a d-min stain endpoint when they are exposed to light on display than would be the case if they were stored in the dark. Because of this discrepancy, it may not be possible to mathematically integrate dark storage data and light stability data insofar as yellowish stain is concerned.

2) **Light-induced stain which occurs as a result of exposure to light during display.** With high-intensity accelerated light exposure tests, there is frequently a reciprocity failure with both chromogenic and inkjet prints that results in significantly higher levels of stain occurring at the lower illumination level (for example, 35 klux vs. 1.0 klux for equivalent klux hours of exposure). As discussed previously, exposure to light during display may result in much higher rates of stain formation when prints are subsequently stored in the dark. It is clear from tests with many different types of media that exposure to UV radiation (for example, the 313 nm and 365 nm emissions of bare-bulb cool white fluorescent lamps) can greatly increase the rate of light-induced staining that occurs in dark storage. Tests are currently in progress with UV-absorbing filters to determine what improvement might be gained. Further complicating the situation, as shown in Figure 5, is that in many cases light-induced stain is relatively unstable and may be "bleached" by further exposure to light. In addition, as shown in Figure 6, after light-induced yellowish stain that occurs in the dark has been bleached by further exposure to light, additional stain can be generated after the print is once again placed in the dark.

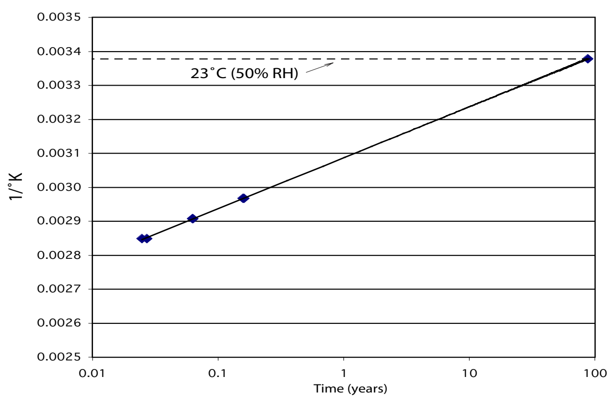

Figure 3. An Arrhenius test with a matte surface inkjet paper in which the data have been extrapolated to storage at 23°C and 50% RH for 88 years before the first d-min stain parameter listed in Table 1 is predicted to be reached. The test was conducted at five temperatures between 50°C and 78°C at 50% RH. Only the highest three of the temperatures had reached the first failure point at the time of this writing.

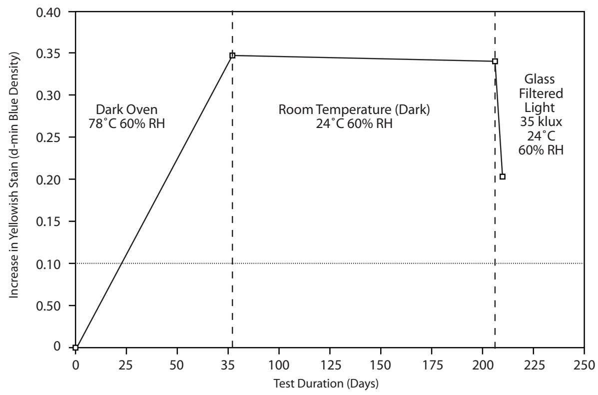

Figure 4. A microporous inkjet paper printed with pigmented inks and placed in a dark oven at 78°C and 60% RH for 35 days developed a very high stain level. After room temperature storage in the dark for 175 days, the print was exposed to 35 klux glass-filtered illumination and the yellowish stain began to rapidly fade (lose density). With this and most other materials tested, a 0.10 blue d-min increase, marked with a thin dotted line, is the first d-min failure to be reached because it results in a 0.10 color imbalance between blue density and red density (see Table 1).

3) **"Apparent stain" caused by loss of activity of fluorescent (optical) brighteners that are present in many inkjet materials.** Experiments have shown that brighteners can lose activity – partially or completely – either as a result of exposure to light and/or high-temperature dark incubation. As a result, papers may appear to have "yellowed." From a permanence point of view, it would be best if fluorescent brighteners were not used in the manufacture of inkjet photographic papers (both Epson and Arches have recently introduced 100% cotton-cellulose-base fine art papers which are free from fluorescent brighteners). In recent years, chromogenic papers have been made with UV-absorbing interlayers and overcoats and this prevents brighteners that might be present in the base paper from being activated by UV radiation.

4) **Stain caused by exposure to air pollutants and other environmental contaminants.** The dry gelatin of traditional

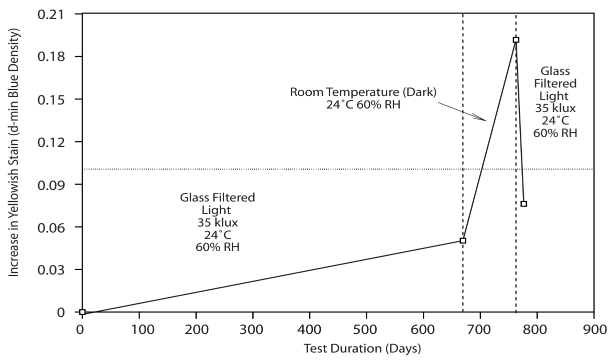

Figure 5. Light-induced "dark staining" of a glossy microporous inkjet paper printed with pigmented inks. After exposure to glass-filtered 35 klux fluorescent light for 675 days, the paper rapidly yellowed in the dark. Upon further exposure to 35 klux light, the stain was quickly bleached and no longer exceeded the d-min stain color balance criteria limit.

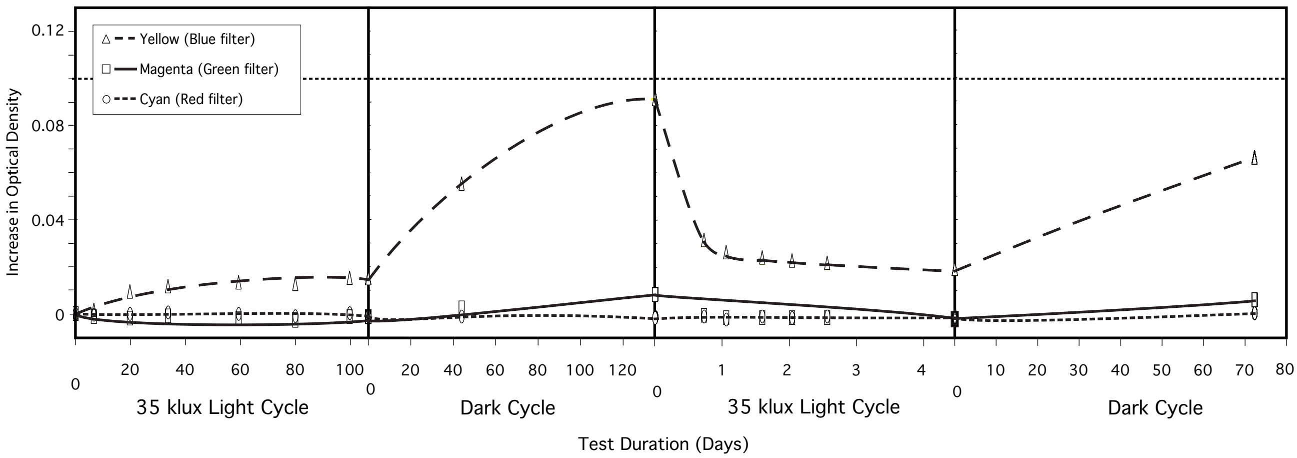

Figure 6. Light-induced "dark staining" of a semi-gloss microporous inkjet paper printed with pigmented inks. After exposure to bare-bulb 35 klux fluorescent light for 110 days, the paper rapidly yellowed in the dark. Upon further exposure to 35 klux light, the stain was significantly bleached in less than 24 hours. But during an additional 70 days of storage in the dark at room temperature, the stain level began increasing once again.

color photographic prints offers significant protection from the effects of airborne pollutants. In contrast, inkjet papers must be highly absorbent in order to absorb the ink immediately when it contacts the print surface in order to prevent spreading or "pooling" of the droplets. Unfortunately, inkjet papers – especially microporous papers – remain highly absorbent after the prints are dry. Unless protected from the atmosphere by glass or plastic sheet when displayed or kept in suitable albums or other storage materials, prints may develop stains over time.

This author and others have observed that certain matte-coated fine art inkjet papers may develop either subtle or very bright yellow stains as a result of contact with corrugated cardboard, brown kraft wrapping paper, and packaging tapes with pressure-sensitive adhesives (substances from which appear to pass through packaging paper). This type of stain has also been observed with prints made with these papers that have been mounted with many current brands of dry mount tissues – the stain may become apparent in the days or weeks after mounting. The mechanism causing this type of stain formation is not understood; however, this type of stain is extremely unstable to light and may be bleached to the point where it is no longer visible after exposure to bright light for only minutes or up to a few hours. Because the stain is so unstable to light, it has been seen only on prints stored in the dark and not with those on long-term display. Bienfang Adhesives ClearMount,[8] a thermal dry mount tissue that was recently introduced by the Hunt Corp., is claimed by the manufacturer to be free of this problem. Bugner has reported that nitrogen oxides (but probably not ozone) may cause inkjet papers to form yellowish stain.[9] Mizen and Mayhew have reported that corrugated cardboard and manila paper file folders could produce yellowing when in contact with some inkjet papers.[10] It was also reported that inkjet papers may absorb antioxidants such as BHT (frequently present in polyethylene and polypropylene) which, over time, may produce yellowing in some inkjet papers.

Coatings and laminates for inkjet prints and traditional color photographs may offer significant protection from many common sources of stain. However, these products must be individually evaluated with each ink/media combination because there is the possibility that the laminates and their adhesives, as well as solvent or water-based coatings applied after printing, could themselves cause stain formation over time.

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