Yellowish Stain Formation in Inkjet Prints and Traditional Silver-Halide Color Photographs

Henry Wilhelm
Wilhelm Imaging Research, Inc.
Grinnell, Iowa U.S.A.

Abstract

Inkjet printing of photographs using both dye-based and pigmented inks has become the most popular form of 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.[1] Stain behavior for representative inkjet papers as well as for selected traditional chromogenic ("silver-halide") color photographs are discussed. Using data obtained from high-intensity 35 klux tests, potential stain formation and fluorescent 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 (Figure 1). Many examples from this period studied by this author now have d-min blue densities actually *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 (non-developed) 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 has continued to be a problem for chromogenic prints. As shown in Figures 2–4, 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.[2]

Color conversion to grayscale (white reference on left) | **Scanner red channel [cyan] (d-min red density: 0.14)** | **Scanner green channel [magenta] (d-min green density: 0.26)** | **Scanner blue channel [yellow] (d-min blue density: 0.93)**

Figure 1. Typical of Kodacolor prints produced by Kodak during the period following their introduction in 1942 until around 1953, this print, which was made in 1950 and stored in the dark for 53 years, now exhibits an extremely high level of yellow/orange stain. This type of dark storage (thermal) stain is primarily caused by gradual discoloration of the residual magenta-dye-forming coupler that remains in the prints after the completion of the standard processing and washing procedure. Because the print had to be reproduced as a monochrome image for this IS&T publication, the original very stained color image was digitally converted to channel-separated monochrome images with Adobe Photoshop 7.0. The white reference strip placed on the left of each image is a d-min sample of modern Kodak Ektacolor Edge 7 Paper processed in 1999 and, when measured in 2003, had d-min densities of 0.09 [R]; 0.09 [G]; 0.07 [B] (Status A densitometry).

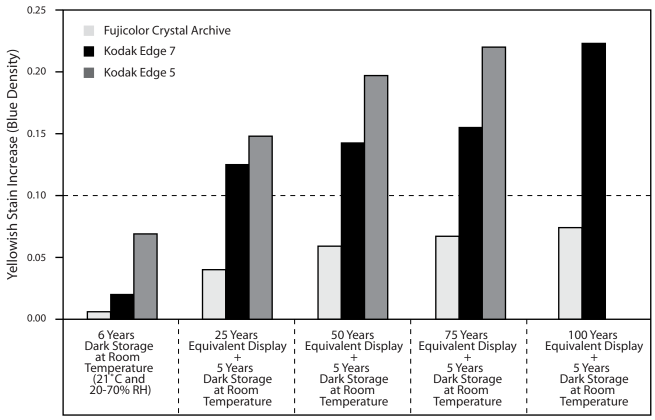

Figure 2. Light-induced "dark staining" with Fujicolor Crystal Archive Paper, Kodak Edge 7 Paper, and Kodak Edge 5 Paper. The three papers were exposed to the equivalent of 450 lux for 12 hours per day for the stated time periods before being placed in the dark for 5 years (100 year light exposure data for Edge 5 were not available). Nearly all of the yellowish stain occurred during the dark storage period.

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 both companies introduced enhanced-stability, low-stain color papers in the early 1990's. 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, Noritsu, Agfa, Konica, and other companies, chromogenic color papers such as Fujicolor Crystal Archive and Kodak Generations Paper are now extensively used for printing digital camera files, either directly from camera memory cards brought to retail stores by consumers, or from CD's, ZIP disks, or files sent to the retailer via the Internet.

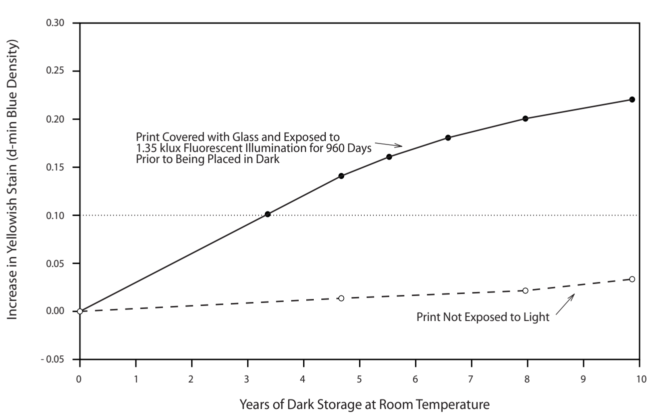

Figure 3. Light-induced "dark staining" of Ektacolor 74 RC Paper (initial type: 1977–82). Yellowish staining occurred at a much more rapid rate after a print was exposed to light for 960 days and then placed in the dark than it did in an identical print that was never exposed to light. Both prints were stored in the same environment.

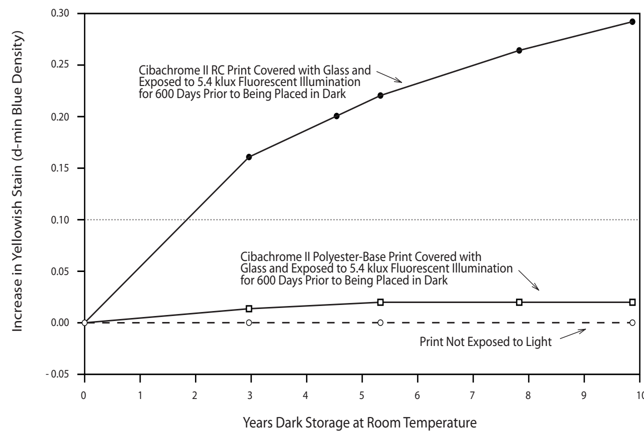

Figure 4. Ilford Cibachrome II RC paper suffered a very large increase in yellowish stain during dark storage after a period of light exposure. Only negligible staining occurred with the glossy, polyester-base version of Ilford Cibachrome II (Ilford Cibachrome was renamed Ilford Ilfochrome in 1991). It is not yet known if TiO_2 pigmented polyethylene-coated RC paper supports may similarly contribute to long-term light-induced yellowish stain formation with RC inkjet photographic papers.

Inkjet Photographic 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 now used extensively by professional photographers and photo labs.

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 Applicable Accelerated Test Methods

There are a number of potential types and causes of yellowish stain formation in inkjet prints and in traditional color photographs; some, such as light-induced and thermally-induced staining, may affect both types of prints while others are specific to inkjet prints.

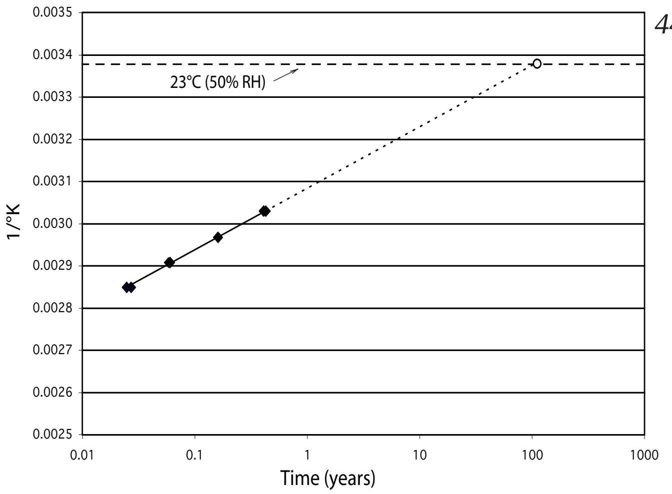

Figure 5. An Arrhenius test with a matte surface inkjet paper in which the data have been extrapolated to storage at 23°C and 50% RH for 110 years before the first d-min stain parameter listed in Table 1 is predicted to be reached. The test was conducted at five temperatures between 50°C and 78°C at 50% RH. At the time of this writing, the highest four of these temperatures had reached the first criteria failure point.

Thermally-Induced Yellowish Stain Occurring 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.[3] 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).[4] Stain estimates for chromogenic papers have been published since the early 1990's by Fuji (most recently in an article Shibahara and colleagues[5]) and by Konica. Limited data have also been provided by Kodak.[6,7] Onishi of Epson has applied the Arrhenius test method to a microporous inkjet paper printed with dye-based inks.[8] Wilhelm Imaging Research currently has Arrhenius tests in progress with a wide range of inkjet and other digital printing materials (see Figure 5). 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 445 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 6). 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.

Light-Induced Yellowish Stain Occurring 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 now in progress with UV-absorbing filters to determine what improvement might be gained. Further complicating the situation, as shown in Figure 7, 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 9,

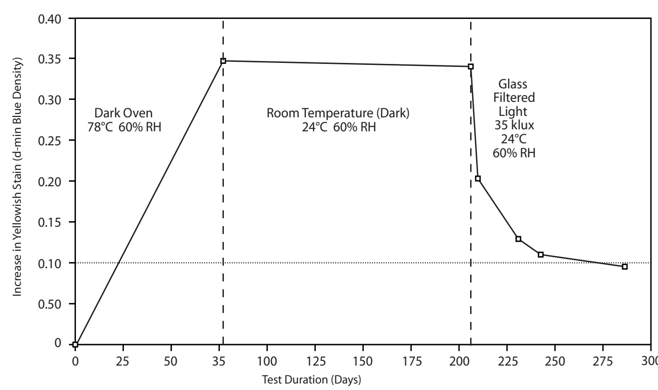

Figure 6. A microporous inkjet paper printed with pigmented inks and placed in a dark oven at 78°C and 60% RH for 35 days developed a very high stain level. After room temperature storage in the dark for 175 days, the print was exposed to 35 klux glass-filtered illumination and the yellowish stain began to rapidly fade (lose density) and soon fell below the stain color imbalance criteria endpoint. 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).

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.

after light-induced yellowish stain that occurred 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. This cycle apparently can be repeated many times.

"Apparent Stain" Caused by Losses in Activity of Fluorescent Brighteners

Fluorescent brighteners (also called "UV brighteners," "optical brighteners," or "optical brightening agents" [OBA's]) are white or colorless compounds added to most inkjet and other papers in order to make them appear whiter and "brighter" than they really are. Fluorescent brighteners absorb ultraviolet (UV) radiation, causing the brighteners to fluoresce (emit light) in the visible region, especially in the blue and green portions of the spectrum. As shown in Figure 8, fluorescent brighteners can lose activity – partially or completely – as a result of exposure to light. Brighteners may also lose activity when subjected to high temperatures in accelerated thermal aging tests and, it may be assumed, in long-term storage in albums or other dark places under normal room tempera-

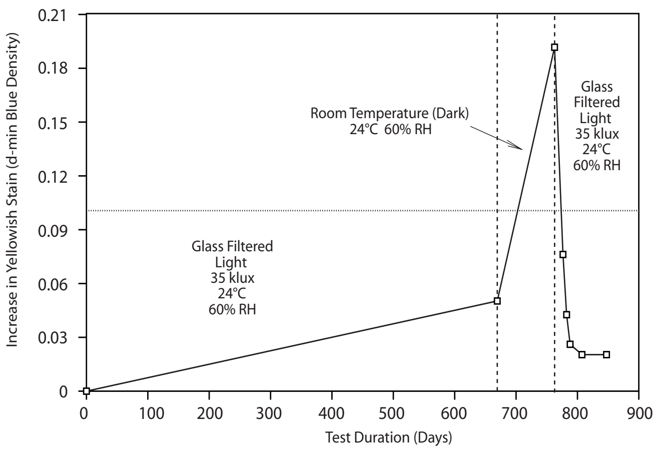

Figure 7. Light-induced "dark staining" of a glossy microporous inkjet paper printed with pigmented inks. After exposure to glass-filtered 35 klux fluorescent light for 675 days, the paper rapidly yellowed in the dark. Upon further exposure to 35 klux light, the stain was quickly bleached and it no longer exceeded the d-min stain color balance criteria limit.

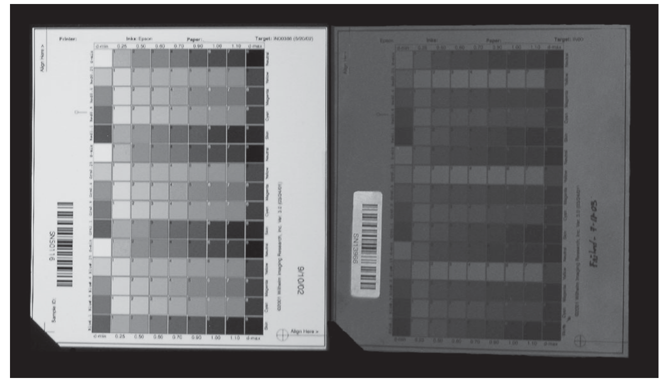

Figure 8. Exposure to light during display gradually degrades fluorescent brighteners resulting in a loss of activity and an apparent yellowing of the paper. In the examples shown here, test target prints made with a matte-coated inkjet paper printed with pigmented inks were photographed illuminated by 365nm UV radiation to visually indicate the level of brightener activity. The print on the left was stored in the dark after printing. The print on the right was exposed to glass-filtered 35 klux fluorescent illumination for 210 days at 24°C and 60% RH, and suffered an almost total loss of brightener activity. Under typical indoor illumination, which contains adequate UV radiation to activate fluorescent brighteners, the print appears somewhat yellowed and not as "white" compared with the print that was kept in the dark. Prints made with high-stability inksets can be exposed to light on display for much longer periods before reaching the first criteria failure endpoint than that required for significant – or even total – degradation of many types of fluorescent brighteners. When image permanence may be an important factor, fluorescent brighteners should be avoided in the manufacture of photographic materials.

ture conditions. With loss of brightener activity, papers will appear to have yellowed and to be "less white." 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. It is the relative UV component in the viewing illumination that determines the perceived "brightening effect" produced by fluorescent brighteners. If the illumination contains no UV radiation (for example, if a UV filter is used in framing a print), fluorescent brighteners are not activated and, comparatively speaking, the paper appears to be somewhat yellowed – and not as "white." This spectral dependency of fluorescent brighteners makes papers containing fluorescent brighteners look different depending on the illumination conditions. It is also possible that brightener degradation products can themselves be a source of yellowish stain. These problems can be avoided simply by not adding fluorescent brighteners to inkjet photographic papers during manufacture (both Epson and Arches have recently introduced 100% cotton-cellulose-base fine art papers which are free from fluorescent brighteners).

Stain Caused by Exposure to Air Pollutants And Other Environmental Contaminants

The dry gelatin of traditional 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 reported 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 when prints made with these papers have been mounted with many current brands of dry mount tissues. The staining became 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 normal display. Bienfang Adhesives ClearMount,[9] 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.[10] Mizen and Mayhew have reported that corrugated cardboard and manila paper file folders could produce

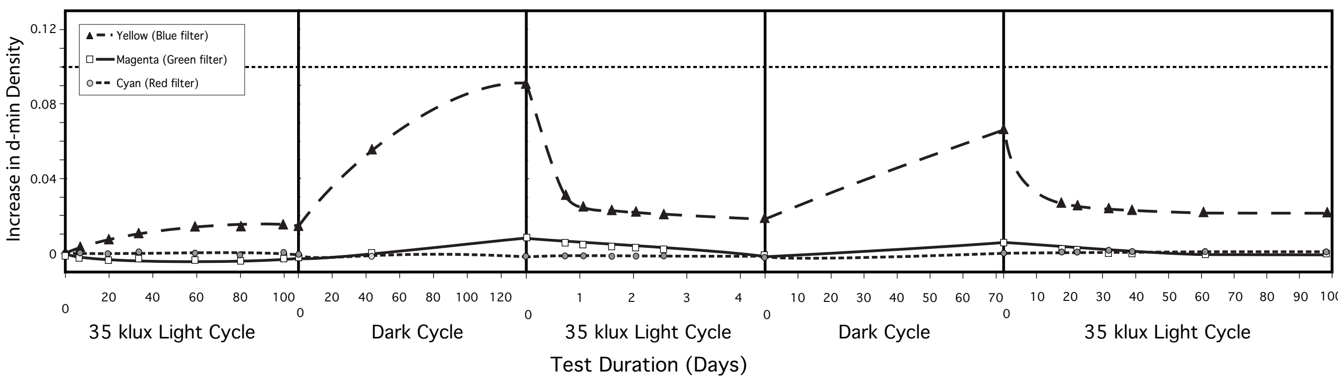

Figure 9. Light-induced "dark staining" of a semi-gloss microporous inkjet paper printed with pigmented inks. After exposure to bare-bulb 35 klux fluorescent light for 110 days, the paper rapidly yellowed in the dark. Upon further exposure to 35 klux illumination, the stain was significantly bleached in less than 24 hours. But during an additional 70 days of storage in the dark at room temperature (24°C, 60% RH), the stain level rapidly increased once again. The sample was then exposed to 35 klux light for 100 days and the stain level dropped back to approximately the same level reached at the end of the first period of light exposure.

yellowing when in contact with some inkjet papers.[11] 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 to inkjet prints or to traditional color photographs after printing, could themselves cause stain formation over time.

Conclusions

Together with light fading, thermally-induced fading, and gas (ozone) fading of dye or pigment inkjet printed images and traditional chromogenic color photographs, it is very important to also evaluate paper stain behavior. Because yellowish stain with many products is unstable to light (subject to light fading) it is not possible to integrate light-stability and dark-stability test data in a simple manner as is now described in ISO 18909 for traditional color photographic materials. Additional research is being conducted at Wilhelm Imaging Research concerning how to best evaluate potential light-induced and thermally-induced yellowish stain formation with short-term, accelerated tests in the context of long-term display and dark storage of both traditional chromogenic photographs, inkjet photographs, and other types of digitally-printed images.

References

1. This paper is an expanded version of a paper published earlier in 2003: Henry Wilhelm, "Light-Induced and Thermally-Induced Yellowish Stain Formation in Inkjet Prints and Traditional Chromogenic Color Photographs," *Japan Hardcopy 2003: Proceedings of the Annual Conference of the Imaging Society of Japan,* pp. 213–216, Tokyo, Japan, June 12, 2003. This document is also available in Adobe Acrobat PDF format: <www.wilhelm-research.com>.
2. Henry Wilhelm and Carol Brower (contributing author), *The Permanence and Care of Color Photographs: Traditional and Digital Color Prints, Color Negatives, Slides, and Motion Pictures,* pp. 69–77, Preservation Publishing Company, Grinnell, Iowa, 1993. The entire 757-page book or any of the book's 20 individual chapters are available in Adobe Acrobat PDF format and may be downloaded at no cost from: <www.wilhelm-research.com>.
3. *ANSI IT9.9–1996, American National Standard for Imaging Media – Stability of Color Photographic Images – Methods for Measuring,* American National Standards Institute, Inc., New York, New York, 1996. In 2004, a revised ISO version of this document is expected to be published under the title of: *International Standard ISO 18909, Imaging materials – Processed photographic colour films and paper prints – Methods for measuring image stability.*
4. Henry Wilhelm, "How Long Will They Last? An Overview of the Light-Fading Stability of Inkjet Prints and Traditional Color Photographs," *Final Program and Advance Printing of Paper Summaries, IS&T's 12th International Symposium on Photofinishing Technology,* pp. 32–37, Orlando, Florida, February 20–21, 2002. Also available in PDF format: <www.wilhelm-research.com>.
5. Yoshihiko Shibahara, Hiroshi Ishizuka, Naotsugu Muro, Yukihiko Kanazawa, and Yoshio Seoka, "Image Stability of Digital Photographic Printing Materials," *Final Program and Proceedings of IS&T's NIP18: International Conference on Digital Printing Technologies,* pp. 330–333, San Diego, California, October 1, 2002.
6. David F. Kopperl, Brian Thomas, and David L. Price, "Some Considerations Around Thermal Yellowing of Color Negative and Reversal Papers," *Journal of Imaging Science and Technology,* Vol. 42, No. 2, March/April 1998, pp. 153–154.
7. Stanton Anderson and David Kopperl, "Limitations of Accelerated Image Stability Tests," *Journal of Imaging Science and Technology,* Vol. 37, No. 4, July/August, 1993, pp. 363–373.
8. Hiroyuki Onishi, Masahiro Hanmura, Hidemasa Kanada, Teruaki Kaieda, "Image Permanence of Ink Jet Photographic Prints," *Final Program and Proceedings of IS&T's NIP17: International Conference on Digital Printing Technologies,* pp. 192–196, Ft. Lauderdale, Florida, October 3, 2001.
9. Bienfang ClearMount thermal dry mounting tissue (recommended press temperature of 88°C [190°F]) for use with pigmented inks and fine art and photography inkjet papers was introduced in January 2003 and is available from Hunt Corporation, Customer Service, P.O. Box 5819, Statesville, North Carolina 28678-5819; tel: 704-872-9511; <www.hunt-corp.com>.
10. Douglas E. Bugner, "A Survey of Factors Influencing the Image Stability of Various Digital Printing Technologies," *Information Management Institute (IMI) 2nd Annual Photographic Quality Digital Printing Conference,* Scottsdale, Arizona, May 1, 2003.
11. Mark B. Mizen and Christopher M. Mayhew, "Influence of Enclosure and Mounting Materials on the Stability of Inkjet Images," *Final Program and Proceedings of IS&T's NIP17: International Conference on Digital Printing Technologies,* pp. 231–234, Ft. Lauderdale, Florida, October 3, 2001.

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