

Filtration and Reciprocity Effects on the Fade Rate of Inkjet Photographic Prints

*Douglas E. Bugner and Christine Suminski
Imaging Materials and Media, Research & Development
Eastman Kodak Company
Rochester, NY 14650 USA*

Abstract

In this study, we examine the effects of filtration and reciprocity on the fade rate of inkjet photographic prints intended for display in the home and/or office environment. Test prints on a variety of ink-receiver combinations were subjected to three different illumination conditions: (a) Plexiglas-filtered 5.4 Klux cool white fluorescent (PLIF), (b) Plexiglas-filtered 67 Klux cool white fluorescent (PHIF), and (c) unfiltered 72 Klux cool white fluorescent (UHIF). The primary color patches, secondary color patches, and neutral density patches were monitored at a density of 1.0 above D_{\min} by status A densitometry at specified intervals of time. Plots of ΔD vs cumulative exposure were fit to either a natural log or linear function, and fade rates were thus determined. The effect of filtration under high intensity lighting conditions and the effect of light intensity (reciprocity) on the different ink-receiver combinations are discussed.

Introduction

With the recent introduction of photographic quality inkjet printers from Hewlett-Packard, Epson, Canon, Lexmark, and Kodak targeted at owners of consumer digital cameras, attention has now focused on improving the image stability and physical durability of inkjet photographic output. In the past, inkjet prints have suffered from a number of image stability limitations, including light fade, waterfastness, dark storage, and image smear at high humidity.

For prints intended for indoor display in a home or office, there is a need to estimate print life with respect to different environmental factors. With respect to light fade, accelerated testing using either unfiltered or glass-filtered high intensity fluorescent lamps has been used in accordance with ANSI Standard IT9.9 to provide an estimate of print life.^{1,2} Two concerns with this methodology are (a) the effect of filtration to remove the UV component of the fluorescent light, and (b) the assumption that there is little or no reciprocity failure between the high intensity accelerated treatment and the ambient intensity lighting conditions that are being modeled. Although Wilhelm¹ has reported on the effects of filtration and reciprocity for traditional silver

halide prints, a similar detailed study has not been reported for inkjet prints. Zinn, et al.² described a study on reciprocity effects for inkjet prints and concluded that reciprocity failure did not appear to be a problem. However, the light intensity was varied by only a factor of five (50 Klux vs 10 Klux), and only one unspecified ink-receiver combination was evaluated under both intensities. Although not stated specifically, it also appears that the fluorescent lights used in this study were unfiltered.

An earlier report³ on the nature of the ambient light in Japanese offices showed that the intensity of a brightly lit office averages only about 0.5 Klux. This is about 50 to 100 times less intense than the accelerated treatment conditions used by Wilhelm and Zinn, et al. Furthermore, because most office lights are covered with either plastic diffusers or reflectors, very little, if any, UV irradiation is present at the surface of the print being displayed.³ Studies of lighting conditions in the home have revealed even lower average light intensities and essentially no UV present at the surfaces of interior walls where prints are typically displayed.⁴

Given the wide variety of inks and receivers available in the marketplace today, we set out to examine the effects of filtration and reciprocity on the fade rate of inkjet photographic prints intended for display in the home and/or office environment. We used four recent inkjet printer models specifically targeted at printing digital photographs in the home. We limited this study to prints made on glossy inkjet papers intended for printing photographs. The types of glossy inkjet paper included: non-porous coatings on resin-coated paper (NPRC), non-porous coatings on white PET film, (NPWF), porous coatings on resin-coated paper (PRC), porous coatings on white PET film (PWF), and porous coatings on plain paper (PPP).

Materials and Methods

Materials

A list of the different inkjet receivers used in this study is given in Table 1. The printers used for this study included the Hewlett-Packard DeskJet 970C, the Epson Stylus Color 900, the Lexmark Z51, and the Canon BJC-8200C. All printers were equipped with the OEM-branded printheads

and inks. For the Lexmark Z51, the optional photo ink cartridge was used in place of the standard black cartridge.

Methods

The test targets used in this study comprised step wedges of cyan, magenta, yellow, red, green, blue, and neutral. Each wedge included four coverages of each color: 25, 50, 75, and 100%. Care was taken to ensure that pure colors were printed wherever possible. For the sample target printed on the DeskJet 970C, which uses a pigmented black ink, the neutral wedge was printed using roughly equal amounts of the cyan, magenta, and yellow inks. Not all receivers were printed on each printer. The test targets were subjected to the treatment conditions summarized in Table 2. Energy vs wavelength plots for the different exposure conditions are shown in Fig. 1. The samples were rotated either manually or mechanically to ensure homogeneous exposure during the course of the study. The test targets were monitored at the time intervals indicated in Table 2 by status A densitometry (Gretag/Macbeth Spectro Scan T 3.273 spectrophotometer/colorimeter). In a few instances, additional readings were taken at longer times in order to achieve a 20% density loss in at least one color. An extra set of test targets was kept in the dark under ambient conditions and monitored for any change in density during the course of the study. Changes are reported as density loss (% Δ D). An unprinted area (D_{\min}) of the test target was also monitored, and % Δ D was corrected for D_{\min} .

At each time interval, plots of % Δ D vs initial density (D_0) were made for each primary color, secondary color, and neutral density. For the % Δ D plots of the secondary colors, each of the two primary colors that comprise the secondary color were plotted separately. For the neutral density wedge, all three primary colors were plotted. From these plots, % Δ D for each color was interpolated to $D_0 = 1.0$ above D_{\min} , and this value was plotted against cumulative exposure expressed in terms of Klux-hrs for each data set. For almost all cases, either a natural log or linear least squares equation provided a good fit through each data set ($R^2 > 0.95$). From the % Δ D vs cumulative exposure equations, the cumulative exposure at % Δ D = 20 was calculated for each data set.

The filtration factor, F , is defined as the ratio of the cumulative exposure at % Δ D = 20 under PHIF conditions to the cumulative exposure under UHIF conditions for the same primary color in a specific color patch. Likewise, the reciprocity factor, R , is defined as the ratio of the cumulative exposure at % Δ D = 20 under PHIF conditions to the cumulative exposure under PLIF conditions for the same primary color in a specific color patch.

Results and Discussion

General Observations

In this study, we tested nearly 100 distinct ink-receiver combinations. For each printer-ink set, the kinetics of fade varied widely as a function of the receiver under each of the exposure conditions. As noted above, the vast majority of

ink-receiver combinations faded by either logarithmic (1st order) or linear (2nd order) kinetics, suggesting at least two different mechanisms of dye fade. This will be discussed further below. For the HP, Epson, and Canon ink sets, either the cyan or magenta inks faded the fastest, depending on the specific receiver and exposure conditions. For Lexmark, the yellow ink was by far the weakest.

Table 1. Glossy inkjet receivers used in this study.

Brand	Description	Type
Kodak	Premium Picture Paper	NPRC
Kodak	Picture Paper	PPP
HP	Premium Photo Paper C6039A	NPRC
HP	Prem. Plus Photo Paper C6831A	NPRC
HP	Prem. Glossy IJ Paper C3833A	NPWF
HP	Brochure & Flyer Paper C6955A	PPP
Agfa	Glossy Photo IJ Paper	NPRC
Polaroid	IJ Photo Paper 74100	NPRC
Ilford	Glossy Photo Paper DTPGP9	NPRC
Imation	Photo Quality Paper	NPRC
Epson	Photo Paper S041141	PPP
Epson	Photo Qual. IJ Paper S041124	PPP
Epson	Glossy White Film S041072	PWF
Canon	Glossy Photo Paper	PUP
Konica	Photolike QP Glossy Med. Wt.	PRC
Great White	Glossy Photo Paper	NPRC
Hammermill	Jet Print Photo	PPP
Mafco	Royal Brites 71064	PPP
Asahi Glass	Pictorico	PPP
Champion	High Gloss IJ Paper HGJ5011	PPP
Arkwright	Universal Glossy Photo Paper	NPRC
TST/Impresso	Photo Jet Inkjet Paper 1420	PPP

Table 2. Exposure conditions used for this study.

Condition	UHIF	PHIF	PLIF
Description	Unfiltered High Intensity Fluorescent	Plexiglas-Filtered High Intensity Fluorescent	Plexiglas-Filtered Low Intensity Fluorescent
Bulb Type	GE F72T12/CW	GE F72T12/CW	GE FT96T12/SP41 plus Sylvania FT96T12/D41
Intensity (Klux)	72	67	5.4
UV (W/m^2)	2.0	0.1	0.01
Blue (W/m^2)	18.3	15.5	1.66
Green (W/m^2)	41.2	37.7	3.06
Red (W/m^2)	21.2	19.7	1.98
Temp.	18-22°C	18-22°C	18-22°C
RH	45-55%	45-55%	45-55%
Readings	1,2,4,7,14 days	1,2,4,7,14 days	4,7,14,28, 56 days

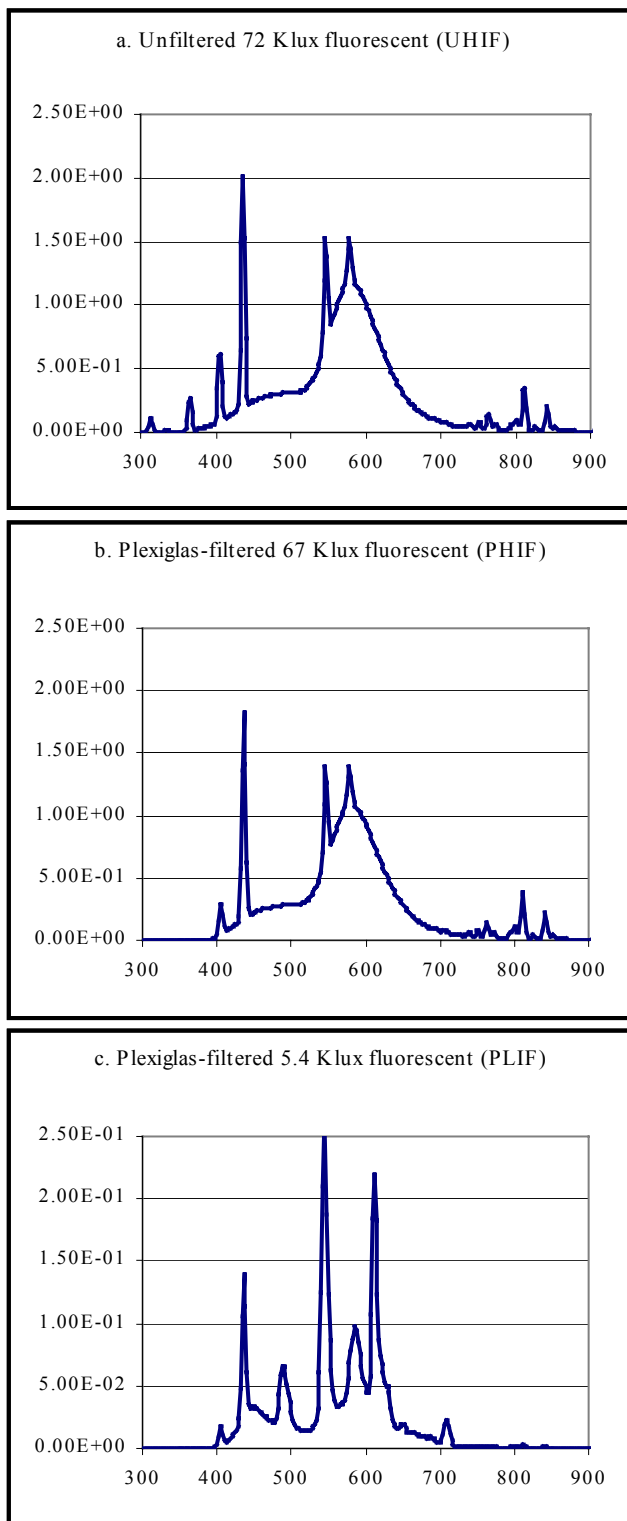


Figure 1. Spectral energy distributions for the exposure conditions used for this study. The X-axis is wavelength in nm, and the Y-axis is energy density in $W/m^2/nm$.

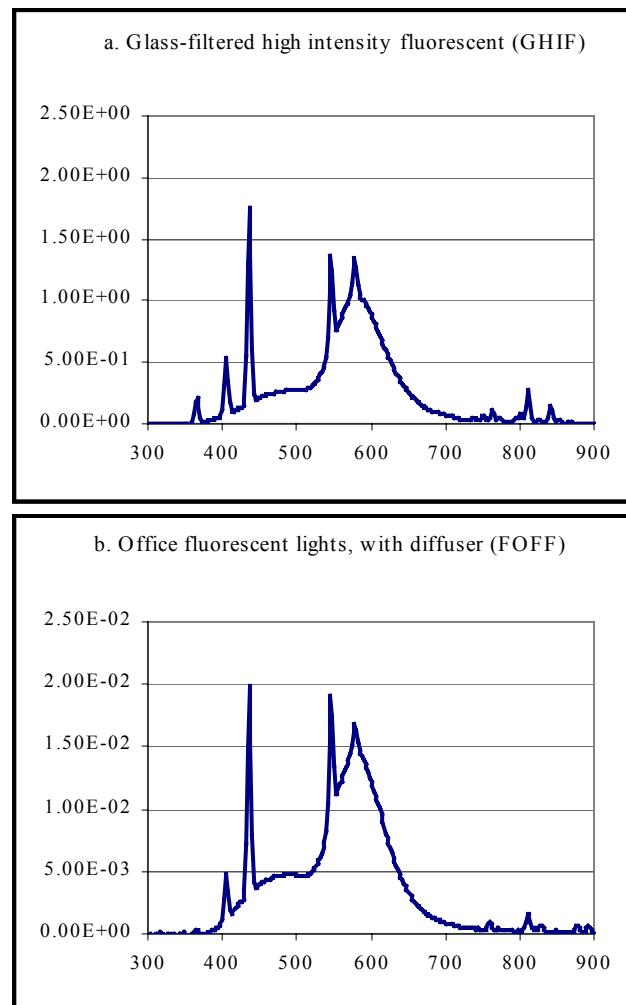


Figure 2. Spectral energy distributions for (a) soda lime glass-filtered high intensity fluorescent lights and (b) office fluorescent lights covered with a standard plastic diffuser. The X-axis is wavelength in nm, and the Y-axis is energy density in $W/m^2/nm$.

Evidence of “catalytic fade”⁵ was observed in some of the secondary and neutral wedges, but it, too, was highly variable as a function of the receiver. We also observed the opposite effect for a few of the ink-receiver combinations, i.e., the magenta in combination with cyan in the blue wedge for the Epson 900 inks on several receivers was significantly more stable than the pure magenta by itself. The reason for this enhanced stability is unclear at this time.

Filtration Effects

The spectral energy distributions for the three different treatment conditions used in the study are shown in Fig. 1. For reference, the analogous spectra for 6-mm soda lime glass-filtered high intensity fluorescent lights (GHIF) and for a typical office lit by fluorescent lights covered by a plastic diffuser (FOFF) are shown in Fig. 2. It can be seen that the unfiltered fluorescent lights (Fig. 1a) emit a significant amount of UV radiation with peaks at 313 and

366 nm. Filtration with glass (Fig. 2a) removes the emission at 313 nm but not the emission at 366 nm.

In contrast, the office spectrum (Fig. 2b) shows essentially no UV content. This is consistent with the previously mentioned study⁴ of office lighting in Japan. In fact, the published spectrum in reference 4 is virtually identical to Fig. 2b. The PHIF spectrum (Fig. 1b), albeit at a higher energy output, is a much closer match to the office spectrum than either the UHIF or GHIF spectrum.

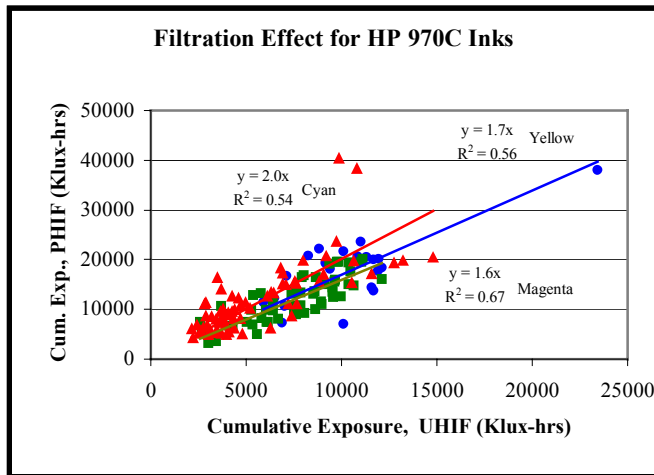


Figure 3. Correlation of the cumulative exposures to reach 20% fade from a 1.0 initial density between PHIF and UHIF conditions for the HP 970C ink set.

Figure 3 is a plot of the cumulative exposures to reach 20% fade under PHIF vs UHIF (filtered vs unfiltered) exposure conditions for the HP 970C inks on 20 receivers. Each primary color was monitored by itself and as its component of the secondary colors and the neutral wedge. In order to be included in the plot, the 20% fade point must have been reached after the first reading and within 10% of the latest reading for the same color wedge under both conditions, and R^2 for the plots of $\% \Delta D$ vs cumulative exposure must have been greater than 0.95. In 140 out of 141 data points that met these criteria, the rate of fade was significantly faster under the unfiltered condition. As can be seen from Fig. 3, there is generally a poor correlation between PHIF and UHIF results, with R^2 ranging from 0.54 to 0.67. The correlation did not improve significantly when the porous and non-porous receivers were plotted separately. The slopes of the lines in Fig. 3 indicate that the filtration factor, F , ranges between 1.6 and 2.0. In other words, inkjet prints fade approximately 2 times faster under unfiltered than under filtered fluorescent lights of comparable intensity. Similar results with respect to the filtration effect were observed for the other printer-ink sets across the same range of receiver types.

In conjunction with the foregoing discussion of the differences in the spectral energy distributions, these results suggest that unfiltered high intensity fluorescent lamps may not be a valid predictor of light fade under ambient conditions. Even glass-filtered fluorescent results should be viewed with caution due to the presence of the strong 366-

nm emission that is not observed in the typical office spectrum. In either case, without factoring in reciprocity effects discussed below, the use of unfiltered or glass-filtered high intensity fluorescent exposure conditions would generally lead to faster fade rates and understated print life estimates.

Reciprocity Effects

Figures 1b and 1c compare the spectral energy distributions for the Plexiglas-filtered high intensity (PHIF) and the Plexiglas-filtered low intensity (PLIF) exposure conditions. The detailed shapes of the curves are quite different due to the use of different types of cool white fluorescent bulbs. However, when one looks at the relative energy output in going from the UV \rightarrow blue \rightarrow green \rightarrow red regions of the spectrum (see Table 2), the energy distribution is actually quite similar, with approximately a factor of 10 difference in energy density across the spectrum.

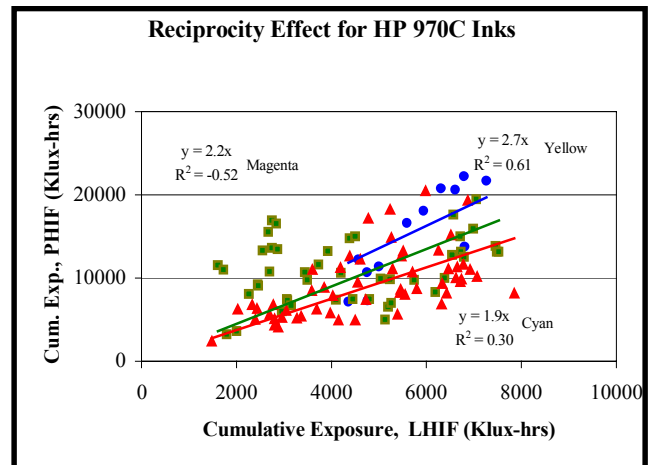


Figure 4. Correlation of the cumulative exposures to reach 20% fade from a 1.0 initial density between PHIF and PLIF conditions for the HP 970C ink set.

Figure 4 is a plot of the cumulative exposures to reach 20% fade under PHIF vs PLIF (67 Klux vs 5.4 Klux) exposure conditions for the HP 970C inks, analogous to Fig. 3. As with Fig. 3, the correlation is generally poor. The slopes of the lines in Fig. 4 indicate that the fade rate is about 2 to 3 times faster on average under the lower intensity exposure conditions. When the porous receivers are viewed separately from the non-porous receivers, the reciprocity factor, R , averages about 3 for the porous receivers and less than 2 for the non-porous receivers. The magenta ink on the porous receivers is noticeably more sensitive to reciprocity effects ($R_{ave} = 3.8$) than the yellow or cyan inks. It should be noted, however, that only a two of the HP 970C yellow containing wedges (yellow, green, red, or neutral) on non-porous receivers have yet reached the 20% fade point under both PHIF and PLIF conditions.

For the Epson 900, Canon 8200, and Lexmark Z51 ink sets, the differences between porous and non-porous receivers were more pronounced, especially for the cyan

inks. For the Epson 900 cyan ink, for example, only two of 32 possible⁶ 20% fade points were reached for the non-porous receivers under the PHIF condition and none under the PLIF condition. However, for the porous receivers, 14 of 44 cyan 20% fade points were reached under the PHIF condition, and 33 of 44 were reached under the PLIF condition. Of these, there were 13 in common, and $R_{ave} = 7.2$. For the Epson 900 magenta ink, more 20% fade points were reached for both types of receivers, and the porous receivers were again more sensitive to reciprocity effects ($R_{ave} = 2.5$) than the non-porous receivers ($R_{ave} = 1.5$). As with the HP 970C ink set, not enough yellow 20% fade points have been reached to draw meaningful conclusions at this point. We will continue to monitor the samples under both PHIF and PLIF conditions.

One possible explanation for the higher reciprocity effect for porous receivers is their higher permeability to air. If a dye fades by a photo-oxidative mechanism, which is not uncommon for the anionic dyes used in inkjet inks, then the rate of fade will be a function of the localized oxygen concentration. At high enough light intensity (photon flux), or with less oxygen-permeable non-porous inkjet receivers, the oxygen concentration in the immediate vicinity of the dye would be the limiting reagent. At lower light intensities, especially with oxygen-permeable porous receivers, the observed rate of fade might be expected to increase, as observed.

An alternate explanation would be that the dyes are being slowly oxidized by a parallel, non-photonic process, due to the presence of air pollutants such as ozone.⁷ Although such a process cannot be totally ruled out in the present study, the fact that "keeper" prints kept in the dark under similar environmental conditions did not exhibit any measurable dye fade during the course of this experiment is inconsistent with this mechanism.

Summary

The use of unfiltered, high intensity fluorescent lights to accelerate the light fade of inkjet photographic prints may not reflect what actually happens under ambient conditions. Unfiltered fluorescent light contains strong ultraviolet emissions not typically present in the home or office environment. Inkjet dyes fade at different rates and possibly by different mechanisms when subjected to unfiltered, UV-rich fluorescent lights. The correlation with Plexiglas-filtered fluorescent light, which removes most of the UV radiation, is quite poor.

Reciprocity effects also are a concern when using high intensity light, filtered or unfiltered. This is especially true for inkjet receivers that are porous. Dyes that are prone to photo-oxidation in combination with oxygen-permeable porous receivers are a possible explanation for the large observed reciprocity effects. Regardless of the mechanism,

print-life estimates for photographic inkjet prints based solely on the use of highly accelerated light fade conditions, especially those that contain significant UV radiation, should be viewed with caution.

Acknowledgments

The authors wish to acknowledge the assistance of David Price, Pam Hill, and Tom Nicholas for their help in carrying out this study.

Notes and References

1. H. Wilhelm, *The Permanence and Care of Color Photographs*, Preservation Publishing Company, Grinnell, Iowa, 1993, pp. 61-100.
2. E. Zinn, E. Nishimura, and J. Reilly, *Proc. NIP 15*, pg. 416 (1999).
3. S. Tachikawa, *J. Illum. Eng. Inst. Jpn.*, 59, 86 (1974).
4. S. I. Anderson and R. J. Anderson, *J. Imaging Tech.*, 17, 127 (1991).
5. S. Schuttel and R. Hofmann, *Proc. NIP 15*, pg. 120 (1999).
6. 8 non-porous receiver samples times 4 cyan-containing wedges per receiver (cyan, green, blue, neutral) = 32 possible fade points.
7. Such a mechanism has been proposed to explain the unexpected premature cyan fade for prints made with the Epson 870 printer on the porous Epson Premium Glossy Photo Paper. See for example: <http://www.epson.com/whatsnew/ygtsi/lightfast.html>

Biography

Douglas Bugner received his B.S. in Chemistry from the Ohio State University in 1975, a M.S. in Organic Chemistry from UCLA in 1980, and a Ph.D. in Organic Chemistry from UCLA in 1982. In 1982, Dr. Bugner joined the Chemical Technology Laboratory in the Photomaterials Division of Eastman Kodak. In 1988, he accepted an assignment in the Photoconductor Technology Laboratory, and in 1991, he was appointed manager of the Chemical Technology Lab. In 1993, Dr. Bugner established a research effort in the area of inkjet materials, and the Inkjet Materials Technology Laboratory was formed in 1994, which he headed until 1999. Dr. Bugner is currently Director of Product Delivery, Output Products, Digital and Applied Imaging, Eastman Kodak Company.

In 1994, Dr. Bugner received the Distinguished Inventor Award, and in 1997, he was selected to participate in the Executive Development Program at the Tuck School of Business at Dartmouth. He currently holds 50 U.S. Patents, and has authored over 20 scientific publications.