

## OPTICAL BRIGHTENERS IN BLACK-AND-WHITE PHOTOGRAPHIC PAPER: APPEARANCE AND DEGRADATION

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**ABSTRACT**—Forty-five optically brightened black-and-white photographic papers from 12 manufacturers spanning 1956–2006 were studied to evaluate the brightener's impact on appearance and its light sensitivity under simulated daylight conditions. The appearance tests showed both small and large changes in appearance when the optical brightener was activated by inclusion of UV in the illuminating light source. All papers showed a decrease in the Yellowness Index value upon brightener activation, indicating a change in appearance to a color that is whiter than its un-brightened version. Three papers that were originally warm white in appearance, however, remained somewhat yellow in color even with activation of their optical brighteners. All of the 45 papers experienced some optical brightener loss as a result of prolonged exposure to simulated daylight with UV wavelengths included; many also experienced other color changes such as bleaching or yellowing of the paper substrate and loss of a chromophore at 570 nm. All papers experienced color change rates similar to that of Blue Wool Standard 3 or 4 when exposed to light containing UV and would be considered moderately sensitive to light exposure.

**TITRE**—Agents de blanchiment optique dans les papiers photographiques noir et blanc: leur apparence et dégradation **RÉSUMÉ**—Quarante-cinq papiers photographiques noirs et blancs avec des agents de blanchiment optique provenant de douze fabricants différents et manufacturés entre 1956 et 2006 ont été étudiés pour évaluer l'impact de ces agents sur l'apparence du papier et leur sensibilité à la lumière dans des conditions simulant la lumière du jour. Les tests d'aspect visuel ont démontré des changements d'apparence aussi bien légers que prononcés, lorsque l'agent de blanchiment optique était activé par l'inclusion d'ultraviolet (UV) dans la source lumineuse d'éclairage. Tous les papiers ont accusé une diminution en valeur de l'indice de jaunissement quand les agents de blanchiment étaient activés, indiquant un changement d'aspect vers une couleur qui est plus blanche que sa version sans agents. Trois papiers qui avaient un aspect blanc chaud à l'origine sont cependant restés

quelque peu jaunes en couleur, malgré l'activation de leurs agents de blanchiment optique. Tous les quarante-cinq papiers ont accusé une perte d'agent de blanchiment optique en raison de l'exposition prolongée à une simulation de lumière du jour contenant des longueurs d'onde UV; beaucoup ont également accusé d'autres changements de couleur comme le blanchissement ou le jaunissement du support en papier et la perte d'un chromophore à 570 nm. Tous les papiers ont accusé des changements de couleur semblables à celui de la norme de laine bleue 3 ou 4 une fois exposés à la lumière contenant des ondes UV et seraient considérés comme modérément sensibles à la lumière.

**TITULO**—Abrillantadores ópticos en papeles fotográficos blanco y negro: Apariencia y degradación **RESUMEN**—Cuarenta y cinco papeles fotográficos blanco y negro ópticamente abrillantados, producidos por doce fabricantes entre 1956 y 2006, fueron estudiados para evaluar el impacto del abrillantador sobre su apariencia y sensibilidad a la luz bajo condiciones simuladas de luz de día. Las pruebas de apariencia mostraron pequeños y grandes cambios en apariencia cuando el abrillantador óptico fue activado por la inclusión de UV en la fuente de iluminación. Todos los papeles mostraron una disminución en el valor del Índice de Amarillamiento bajo la activación del abrillantador, indicando un cambio en la apariencia hacia un color que es más blanco que su versión no abrillantada. Sin embargo, tres papeles que eran originalmente blanco tibio en apariencia, permanecieron con un color medio amarillo aún con la activación de sus abrillantadores ópticos. Todos los cuarenta y cinco papeles experimentaron alguna pérdida del abrillantador óptico como resultado de la exposición prolongada a la luz de día simulada que contenía longitudes de onda UV; muchos también experimentaron otros cambios de color tales como blanqueo o amarillamiento del sustrato del papel y pérdida de un cromóforo a 570 nm. Todos los papeles experimentaron tasas de cambio de color similares a *Blue Wool Standard* (las del Estándar de Lana Azul) 3 ó 4 cuando se expusieron a luz con contenido de UV, y se considerarían

SANDRA A. CONNORS-ROWE, PAUL M. WHITMORE,  
AND HANNAH R. MORRIS

como moderadamente sensibles a la exposición de luz.

**TÍTULO**—Branqueadores ópticos em papel fotográfico preto-e-branco: aparência e degradação  
**RESUMO**—Quarenta e cinco papéis fotográficos preto-e-branco branqueados de 12 fabricantes, produzidos entre 1956 a 2006, foram estudados para avaliação do impacto do branqueamento em sua aparência e sensibilidade à luz sob condições simuladas da luz do dia. Testes mostraram pequenas e grandes alterações na aparência do papel quando o branqueador óptico foi ativado através da inclusão de UV na fonte luminosa. Todos os papéis mostraram diminuição de valor no índice de amarelo no branqueamento, indicando mudança na aparência para uma cor mais branca do que a versão sem o branqueamento. Entretanto, três papéis de aparência originalmente branca permaneceram um tanto amarelos mesmo com o branqueador óptico. Todos os 45 papéis sofreram algum tipo de perda no branqueamento como resultado da exposição prolongada à luz do dia simulada com ondas ultravioletas; muitos também apresentaram outras mudanças de cor, como descoloração ou amarelamento da base do papel e perda de coloração a 570 nm. Todos os papéis apresentaram taxas de mudança de cor similares às do padrão *Blue Wool 3* ou *4* quando expostos à luz com UV e podem ser considerados moderadamente sensíveis à exposição à luz.

## 1. INTRODUCTION

The introduction of optical brighteners (i.e., fluorescent dyes that absorb UV radiation and re-emit visible light in the blue region of the spectrum) in the early part of the 20th century fulfilled a consumer desire for whiter and brighter products. Starting with the textile and paper industries, optical brightener use eventually moved to the production of photographic paper, a trend illustrated in a recent survey of historic papers (Messier et al. 2005). Typical viewers tend to associate slight blueness with whiteness, so that a perceived “ideal” white reflects all incident light but also includes additional blue light to create a blue-white appearance (Altherr 1965; Bureau 1979). Optical brighteners achieve this blue-white appearance through fluorescence—the absorption of radiation followed by its re-emission at longer wavelengths. To act as a brightener, a compound absorbs UV radiation and re-emits it in the blue end of the visible spectrum

(400–500 nm). The addition of blue light helps adjust for any dullness or yellow color that may be retained by the paper after processing (Gessner 1956; Adams 1959; Bureau 1979).

Manufacturers have employed optical brighteners in all layers of the photographic paper—e.g., paper base, baryta layer, undercoating, emulsion, or protective layer (Fuji Photo Film Company 1971; Hamilton and Sutton 1978). Brighteners used for both writing and photographic papers are almost exclusively water-soluble stilbene derivatives (Murray 1991; Mustalish 2000; Messier et al. 2005), which makes the problem of loss or movement of brightener during development of photographs a concern. Recently, a method of adding optical brightener to the developer has been used in order to boost the final brightened appearance of a print (www.cibasc.com 2005). For these reasons, the brightened appearance of a photographic paper and the long-term stability of the brightener may vary widely between different manufacturers, between various brands of a single manufacturer, or even in a single paper developed in different processes.

The inclusion of brighteners created a new set of conservation concerns for those responsible for the care and exhibition of optically brightened photographs. Optical brighteners have been observed to degrade from prolonged light exposure and are thought to produce yellow degradation products as a result of that light exposure (Murray 1991). Previous work has determined that deterioration of brighteners does not have an adverse effect on paper permanence (Leclerc and Flieder 1992) and that water-based treatments of optically brightened photographs may produce appearance changes because of the movement of water-soluble brighteners (Wetzel 2005). Other, more subjective concerns also arise. For example, it must be determined (1) if it is appropriate to display a historic photograph on brightened paper if it was created prior to the inclusion of optical brighteners in photographic paper (mid-1950s), and (2) if brightened photographs should be displayed with deteriorated brighteners or brighteners that do not function because of the lack of UV in the illuminating light source. Without understanding the impact optical brighteners have on a paper's appearance, the light-sensitivity of the brighteners themselves, and the overall color changes that result in a photographic paper from prolonged light exposure, these concerns cannot be addressed.

The goal of this study is to focus attention on the appearance created by optical brighteners

## OPTICAL BRIGHTENERS IN BLACK-AND-WHITE PHOTOGRAPHIC PAPER: APPEARANCE AND DEGRADATION

in photographic papers and to understand their light-sensitivity. To this end, the contribution that optical brighteners make to the appearance of a photographic paper was quantified. Trends in optical brightener usage by various manufacturers, brands, and dates were also explored; however, variations in appearance that may result from different processing methods were excluded. This study also examined the degradation rate of the optical brighteners when exposed to simulated daylight with UV wavelengths included. Because of the presence of UV-activated fluorescent materials, the preservation methods typically employed for the exhibition of light-sensitive materials—removal of UV from the illuminating light source and reduction in light intensity—will affect the appearance of optically brightened photographic paper. Thus, UV was included in the exposure conditions to determine if inclusion of UV would produce unacceptably fast degradation of the optical brightener. Finally, the overall color change that resulted from prolonged light exposure was determined, and methods for identifying photographic paper with particularly light-sensitive optical brighteners were explored.

### 2. SAMPLE SELECTION

A set of historic photographic papers, representing 12 manufacturers and ranging in date from 1956–2006, was provided for this study by Paul Messier, of Paul Messier LLC, Conservation of Photographs, Works on Paper, and Electronic Media. This set of papers provides examples of most types of optically brightened black-and-white photographic paper that may be found in a museum collection. Because a goal of this work is to determine the extent to which an optical brightener contributes to the appearance of a photographic paper, only papers with visibly perceptible brightener under long-wavelength UV illumination on the recto of the paper were chosen. Also, trends in optical brightener usage were explored based on manufacturer, brand, and date, and therefore multiple papers were chosen from a single manufacturer whenever possible. In order to limit variations in brightener performance from variations in processing methods and unknown environmental factors, only unexposed papers from factory-sealed packages with known manufacturers, brands, and dates were used for this study. The samples provided had been fixed using ammonium thiosulfate, washed in water for 25 minutes, and air-dried (Messier et al. 2005).

Complete information about the final set of 45 paper samples is listed in table 1, including the manufacturer, date, brand, base color, and texture of each paper. For further details on sample selection see the Appendix.

All of the photographic paper samples were analyzed by fluorescence spectroscopy to determine if they contained the same optical brightener. The emission spectra for all the samples were collected and found to have some variation in peak shape and position but essentially had two peaks centered around 415 and 430 nm. However, the excitation spectra showed greater differences and indicated the possibility of different optical brighteners present for the different samples. (Details on spectroscopic analyses are listed in the Appendix).

Because optical brighteners are employed in all layers of the photographic paper, the chemical environment in the solid state may vary for the different samples and can influence the fluorescence excitation and emission spectrum. Therefore, the differences in the spectra may be due to different optical brighteners or to the change in chemical environment. To simplify the chemical system, extracts were taken from each paper sample to remove the optical brightener, and fluorescence excitation and emission spectra were taken of each paper extract solution. Since it is likely that these papers all contain stilbene compounds as brightening agents, solutions of currently available stilbene brighteners known to be used in the photographic paper industry (Tinopal SFP and Leucophor BCF 115) were tested for comparison. Figure 1 shows the fluorescence emission spectrum for the extract of a typical paper sample (Sample 18) and the two standards. The normalized spectra for all three samples shown were identical (as well as all other paper extracts tested) and had peaks located at 413 nm and 433 nm. These results indicate that the optical brightener used for the different paper samples is most likely a stilbene derivative.

Other methods of analysis that are more chemically specific, including Fourier transform infrared spectroscopy (FTIR), electrospray ionization mass spectrometry (ESI-MS), and matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS), were attempted to identify the specific stilbene derivative brighteners. However, in the absence of historically relevant optical brightener reference samples, positive identification of the exact stilbene derivatives was not possible.

SANDRA A. CONNORS-ROWE, PAUL M. WHITMORE,  
AND HANNAH R. MORRIS

Table 1. Summary of Photographic Paper Information for Each Sample, as Available

Paper number	Date	Manufacturer	Brand	Base color	Texture
1	1956	Kodak	Azo	White	Smooth
2	1957	Kodak	Velox	White	Smooth
3	1960	Kodak	Azo	Snow White	Fine Grained
4	1961	Kodak	Velox	White	Smooth
5	1962	Kodak	Azo	Cream White	Rough
6	1962	Kodak	Velox	White	Smooth
7	1962	Kodak	Velox	White	Smooth
8	1963	Kodak	Velox	White	Smooth
9	1970	Kodak	Velox	White	Smooth
10	1974	Kodak	Velox	White	Smooth
11	1975	Kodak	Velox	White	Smooth
12	1976	Kodak	Polycontrast Rapid RC	White	Smooth
13	1977	Kodak	Velox	White	Smooth
14	1978	Kodak	Polycontrast Rapid RC	White	Smooth
15	1981	Kodak	Polycontrast	White	Fine Grained
16	1982	Kodak	Polycontrast Rapid II RC	White	Smooth
17	1982	Kodak	Polyprint	White	Smooth
18	1989	Kodak	Polyfiber	White	Smooth
19	1990	Kodak	Polymax	White	Smooth
20	1994	Kodak	Polycontrast III	White	Smooth
21	1997	Kodak	Portra	White	Smooth
22	1997	Kodak	Supra III	White	Smooth
23	1998	Kodak	Portra	White	Smooth
24	2003	Kodak	Polymax II	White	Fine Grained
25	2004	Kodak	Polymax II	White	Fine Grained
26	1960	Agfa	Brovira	White	
27	1960	Agfa	Brovira	Crystal White	
28	1965	Agfa	Brovira	White	
29	1965	Agfa	Brovira 117	White	Silk
30	1964	AnSCO	Jet	White	Smooth
31	2006	Bergger	Prestige		
32	1998	Cachet	Structura Lux		Linen
33	1962	Dupont	Varigram	White	
34	1969	Dupont	Varilour	White	
35	1990	Forte	Polywarmtone	White	Smooth
36	2006	Forte	Elegance	White	Smooth
37	1985	Ilford	Galerie		
38	1990	Ilford	Ilfobrom		
39	2000	Ilford	Ilfospeed		
40	2006	Ilford	Multigrade	Brilliant White	
41	2006	Kentmere	Fineprint	Brilliant White	
42	1965	Luminos	Proof Paper		Rough
43	1968	Luminos	Portrait	White	Fine Grained
44	2006	Oriental	Seagull	Pure White	Smooth
45	2006	Photospeed	Lith		

## OPTICAL BRIGHTENERS IN BLACK-AND-WHITE PHOTOGRAPHIC PAPER: APPEARANCE AND DEGRADATION

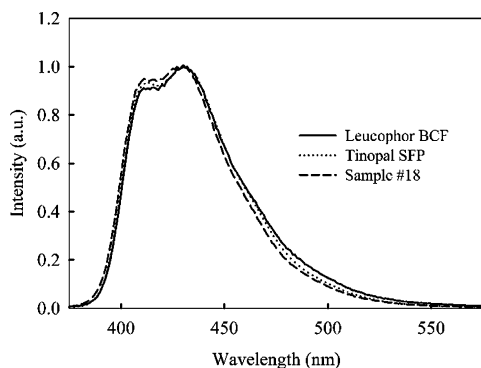


Fig. 1. Normalized fluorescence emission spectra of paper extract (sample 18) and two stilbene containing optical brightener solutions (Leucophor BCF and Tinopal SFP).

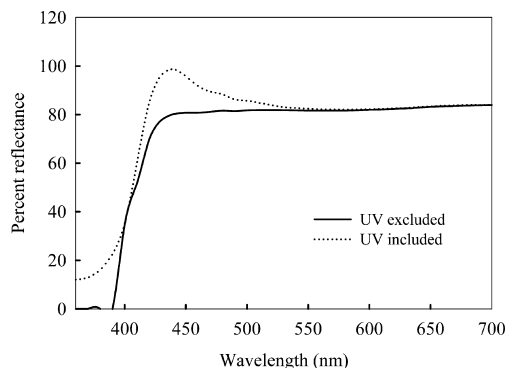


Fig. 2. Reflectance spectra of a typical photographic paper (sample 18) measured with UV included and UV excluded from the light source.

### 3. INITIAL APPEARANCE OF BRIGHTENED PHOTOGRAPHIC PAPERS

#### 3.1 IMPACT OF OPTICAL BRIGHTENERS ON APPEARANCE

When excited by near-UV radiation, optical brighteners emit blue light that should have a perceptible effect on the paper's appearance. The difference between reflectance spectra measured with UV included and UV excluded in the illumination gives an estimate of the contribution of the optical brightener to the paper's appearance. Even those papers with an excitation peak located between 400–405 nm are significantly excited by UV wavelengths. Therefore, the comparison of the two reflectance spectra with UV included and UV excluded is still a reasonable estimate of brightener contribution. Figure 2 shows the reflectance spectra of a brightened photographic paper (paper sample 18) with UV included and excluded from the light source. The fluorescence of the brightener increases the measured reflectance between 400–500 nm with a peak maximum at 430 nm. The impact that this increase in reflectance has on appearance may be described by determining the Yellowness Index value for each spectrum (ASTM 1993). Yellowness is the amount by which an object's color departs from white toward yellow, with a non-fluorescent white reference standard (barium sulfate) having a measured Yellowness Index (YI) value of approximately 11.0. Higher values denote a more yellow color and lower

values denote a blue-white appearance. The Yellowness Index values for the spectra in figure 2 show a change in appearance from YI = 12.6 for the sample measured with UV excluded to YI = 0.5 for the sample measured with UV included, indicating a significant change in appearance from a relatively white paper to a more blue-white color in its brightened state.

In order to excite the optical brightener, a high correlated color temperature (CCT) light source with energy in the UV and blue wavelengths, is required. Therefore, the Yellowness Index is calculated using a high-CCT standard illuminant D65. Although this lighting condition may not be typical for displaying photographs, it was used in this study to demonstrate the greatest possible effect on both appearance and stability of the optical brightener.

The impact of the optical brightener on the appearance of the paper was measured for all of the samples and quantified by the Yellowness Index. Figures 3a and 3b show two values for each paper sample, the YI measured with UV excluded and the YI measured with UV included. These quantities describe the paper's unbrightened and brightened appearance, respectively. The YI of the barium sulfate ( $\text{BaSO}_4$ ) reflectance standard is represented as the horizontal solid line at a value of 11.0 and the color of all the papers will be compared to the white of this standard. For all the papers, there is a decrease in YI when the spectrum is measured with UV included, indicating a change to a whiter appearance when the brightener is activated. The YI values are tabulated in table 2 along with the yellowness index difference,  $\Delta\text{YI}$ , and the color difference,  $\Delta E^*$ , between the unbrightened and brightened appearances.

SANDRA A. CONNORS-ROWE, PAUL M. WHITMORE,  
AND HANNAH R. MORRIS

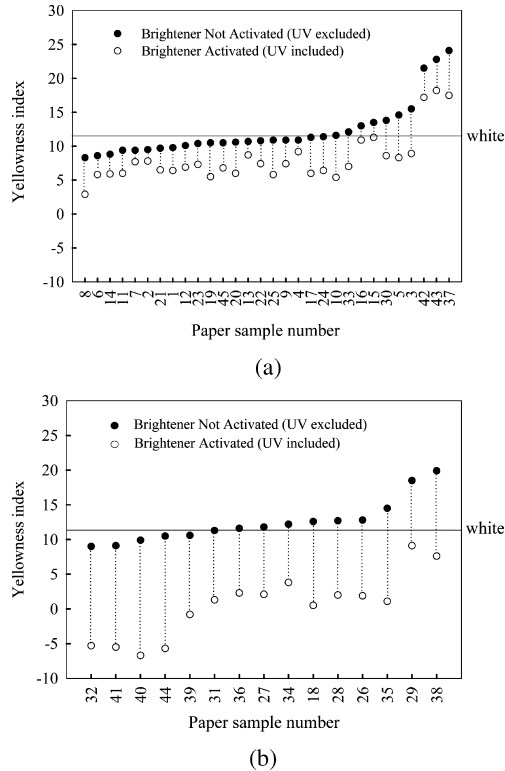


Fig. 3. Range of optical brightener appearance as Yellowness Index (YI) values for the photographic papers with UV included—brightener activated and UV excluded—brightener not activated: (a) small appearance change from optical brightener, (b) large appearance change from optical brightener. The solid line is the YI value for BaSO<sub>4</sub>, a reflectance standard.

The magnitude of the difference in appearance with the brightener activated varies for each sample. The papers have been separated into two groups: those having small color changes from optical brightener being activated ( $\Delta E^* < 5.1$ ), and those showing larger color changes ( $\Delta E^* > 5.9$ ). Most of the 30 paper samples in figure 3a, designated as small color changes, are relatively white compared to the BaSO<sub>4</sub> standard in their unbrightened state (YI values between 8.3–15.5) and appear slightly more white when brightened (YI values 2.9–11.3). For these papers, the contribution from fluorescent emission to their appearance is relatively small ( $\Delta YI$  values 1.7–6.6, listed in table 2). It is interesting to note, however, that three of these paper samples, 37 (Ilford Galerie, 1985), 42 (Luminos Proof Paper, 1965) and 43 (Luminos Portrait, 1968),

retained a somewhat yellow appearance despite their optical brighteners. The unbrightened YI values for these three papers ranged from 21.5–24.1 and only achieved YI values down to 17.2–18.2 when the optical brightener was activated. One thinks of optical brighteners as creating papers that appear unnaturally white, however it seems that in some cases the brightener only slightly diminishes the intrinsic yellow color. These papers remain warm white or buff in color even when brightened.

The paper samples represented in figure 3b show a larger color change from their optical brighteners. Thirteen of these 15 papers appear relatively white in their unbrightened state (YI values 9.0–14.5) and change to a significantly more blue–white color when brightened (YI values –5.3 to 3.8). The final two papers are initially more yellow in color (YI values 18.5 and 19.9 with UV excluded) but change to a white appearance (YI values 9.1 and 7.6) upon brightener activation. The  $\Delta YI$  values for this group range from 8.4 to 16.6, indicating a greater contribution from fluorescent emission than displayed by the papers in figure 3a. For the paper samples in figure 3a the appearance change resulting from deactivation of the optical brightener may be perceptible ( $\Delta E^*$  values  $> 1.0$ ) but is not likely to be objectionable to viewers. However, the appearance change from deactivating the brighteners in the papers in figure 3b is more significant (for most samples  $\Delta E^*$  values  $> 7.0$ ) and may be cause for concern to some viewers. Inclusion of UV in the illuminating light source is necessary to achieve the whiter appearance of these papers and should be considered if the brightened appearance of the paper is preferable to the unbrightened state.

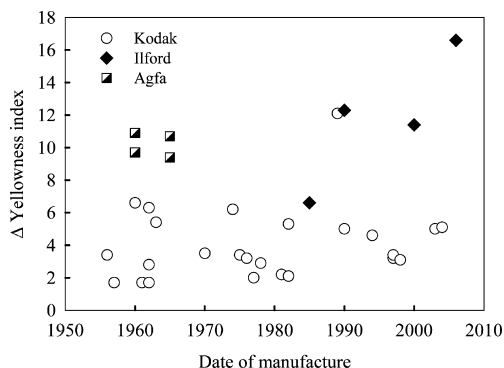
### 3.2 OPTICAL BRIGHTENER USAGE BY MANUFACTURER

The measurement of the appearance changes from activation of an optical brightener allows exploration of possible trends in the extent of paper brightening by manufacturer or date. Figure 4 shows the contribution from fluorescent emission to the appearance of each paper ( $\Delta YI$ , listed in table 2) organized by date of manufacture. Papers made by Kodak, Agfa, and Ilford are highlighted because at least three papers from each of these manufacturers were used for this study. Figure 4 shows that Kodak papers regularly showed a smaller contribution from fluorescent emission to a paper's appearance ( $\Delta YI$  values less than 6.6) compared to

OPTICAL BRIGHTENERS IN BLACK-AND-WHITE PHOTOGRAPHIC PAPER:  
APPEARANCE AND DEGRADATION

Table 2. Appearance Measured as Yellowness Index and the Change in Appearance When Optical Brightener is Activated

Paper number	Yellowness Index- UV excluded	Yellowness Index- UV included	Change in appearance	
			$\Delta YI$	Color difference (CIE L*a*b* $\Delta E^*$ ) - comparing UV included & excluded
Small color change from optical brightener ( $\Delta E^* < 5.1$ )				
1	9.8	6.4	3.4	2.4
2	9.5	7.8	1.7	1.2
3	15.5	8.9	6.6	4.8
4	10.9	9.2	1.7	1.2
5	14.6	8.3	6.3	4.6
6	8.6	5.8	2.8	1.9
7	9.4	7.7	1.7	1.2
8	8.3	2.9	5.4	3.8
9	10.9	7.4	3.5	1.4
10	11.6	5.4	6.2	4.4
11	9.4	6.0	3.4	2.4
12	10.1	6.9	3.2	2.3
13	10.7	8.7	2.0	1.4
14	8.8	5.9	2.9	2.0
15	13.5	11.3	2.2	1.6
16	13.0	10.9	2.1	1.5
17	11.3	6.0	5.3	3.8
19	10.5	5.5	5.0	3.6
20	10.6	6.0	4.6	3.3
21	9.7	6.5	3.2	2.3
22	10.8	7.4	3.4	2.4
23	10.4	7.3	3.1	2.2
24	11.4	6.4	5.0	3.6
25	10.9	5.8	5.1	3.7
30	13.8	8.6	5.2	3.7
33	12.1	7.0	5.1	3.6
37	24.1	17.5	6.6	5.0
42	21.5	17.2	4.3	3.2
43	22.8	18.2	4.6	3.5
45	10.5	6.8	3.7	2.7
Large color change from optical brightener ( $\Delta E^* > 5.8$ )				
18	12.6	0.5	12.1	8.5
26	12.8	1.9	10.9	7.8
27	11.8	2.1	9.7	7.0
28	12.7	2.0	10.7	7.7
29	18.5	9.1	9.4	6.9
31	11.3	1.3	10.0	7.1
32	9.0	-5.3	14.3	9.4
34	12.2	3.8	8.4	5.9
35	14.5	1.1	13.4	9.6
36	11.6	2.3	9.3	6.6
38	19.9	7.6	12.3	9.0
39	10.6	-0.8	11.4	8.1
40	9.9	-6.7	16.6	11.7
41	9.1	-5.5	14.6	10.1
44	10.5	-5.7	16.2	11.4

SANDRA A. CONNORS-ROWE, PAUL M. WHITMORE,  
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## OPTICAL BRIGHTENERS IN BLACK-AND-WHITE PHOTOGRAPHIC PAPER: APPEARANCE AND DEGRADATION

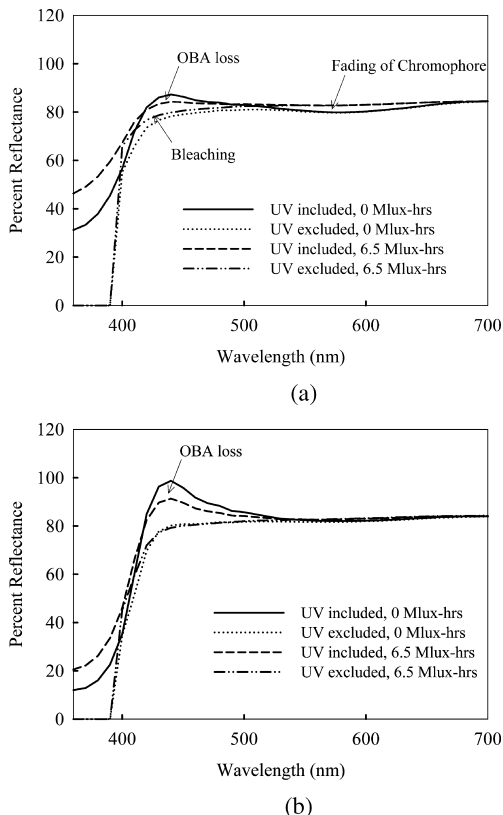


Fig. 5. Reflectance spectra before and after accelerated light aging, with UV included and UV excluded in the instrument source: (a) showing the three types of color change due to light exposure: optical brightener loss, bleaching, and fading of chromophore at 570 nm for paper sample 10, (b) showing only optical brightener loss for paper sample 18.

All paper samples that displayed fading of the chromophore at 570 nm were manufactured by Kodak prior to 1978, with the one exception of paper sample 33 (Dupont Varigram, 1962) which also showed the fading. This spectral feature probably indicates the use of a light-sensitive colorant in the manufacture of these papers.

### 4.2 OVERALL COLOR DIFFERENCE

To determine if these spectral changes resulted in a perceptible change in color, the overall color difference (1976 CIE  $L^*a^*b^*$   $\Delta E^*$  value calculated by comparing the initial and final reflectance spectra

with UV included in the light source) was calculated for each sample (Berns 2000, 69–72). The color difference calculated for each sample is listed in table 3 and ranged from 0.4–7.4  $\Delta E^*$  units. All three types of color change observed during the light exposure can contribute to the color differences. The color change that occurs from optical brightener loss and paper yellowing will cause the photographic paper to appear yellower, while the bleaching of the paper substrate causes the paper to appear whiter. The loss of the chromophore that absorbs around 570 nm should make the paper shift in hue (become less blue, more yellow) very slightly. Therefore, the exposure of the papers to accelerated light aging causes potential reactions that oppose (bleaching of paper substrate) or add to (fading of chromophore at 570 nm or yellowing of paper substrate) the yellowing from brightener loss. As a result, the overall color difference is not an indication of brightener loss, or of the sensitivity of the optical brightener to light, alone. Instead, the measured color changes indicate the net result of all three color change types, which together define the stability of the appearance of these photographic papers.

Figure 6 shows the color change due to accelerated light aging,  $\Delta E^*$ , for all the samples as a function of date of manufacture. Eight samples (12, 14, 21, 23, 29, 33, 38, and 45) experienced color changes that were not perceptible (for this sample set the authors found a just-perceptible color change to be approximately 1.0  $\Delta E^*$  units). The other paper samples listed in table 3 and shown in figure 6 experienced color changes as a result of light aging that would be considered perceptible ( $\Delta E^* > 1.0$ ). Most of these (34 of 37) showed relatively small color changes ( $\Delta E^* \leq 5.0$ ), and only 3 samples (39, 40, and 44) showed larger color changes ( $\Delta E^*$  values 7.0–7.4) that might be considered significant to some viewers. These papers, offered by Ilford and Oriental, seem to be more light-sensitive compared to papers made by other manufacturers. Ten of the eleven samples (1, 2, 3, 4, 5, 6, 7, 8, 26, and 27), all manufactured before 1964, experienced greater overall color change than the majority of samples manufactured after this date (see figure 6). (Samples 1–8 were all manufactured by Kodak.)

The observed degradation rates for the photographic papers were compared to those of ISO Blue Wool fading standards exposed to the same light source. The color difference at the end of the light exposure for Blue Wool 3 and 4 are listed in table 3 and shown as solid lines in figure 6. With all the small differences in overall color change ( $\Delta E^*$ ) between

SANDRA A. CONNORS-ROWE, PAUL M. WHITMORE,  
AND HANNAH R. MORRIS

Table 3. Summary of Accelerated Light Aging for Each Photographic Paper and Blue Wool 3 and 4

Paper Number	Optical brightener loss	Bleaching (+) / Yellowing (-)	Fading	Overall color difference (CIE L*a*b* E*) comparing before and after exposure	Initial optical brightener, $\Delta R_{430}$ (initial)	Final optical brightener, $\Delta R_{430}$ (final)	% Optical brightener loss
1	+	+	+	4.0	4.9	2.0	59
2	+	+	+	3.9	2.4	0.9	65
3	+		+	4.9	9.7	5.0	48
4	+	+	+	2.6	2.5	1.1	57
5	+		+	3.2	9.1	4.5	51
6	+	+	+	3.4	4.0	1.3	66
7	+	+	+	2.9	2.5	0.9	62
8	+		+	4.6	7.9	2.9	63
9	+	+	+	2.6	3.0	1.1	63
10	+	+	+	2.5	9.3	4.6	51
11	+	+	+	2.4	5.2	1.8	65
12	+	+		0.4	5.4	1.5	72
13	+	+	+	2.1	2.8	1.3	54
14	+	+		0.9	4.9	0.6	88
15	+	-		2.0	4.0	1.2	69
16	+	-		2.2	3.7	1.2	66
17	+			1.5	8.3	4.2	49
18	+			3.1	18.6	12.3	34
19	+			1.5	8.4	3.5	59
20	+	+		3.0	7.7	3.2	59
21	+			0.6	5.3	2.2	58
22	+			1.2	5.5	2.2	59
23	+			0.6	5.0	2.2	56
24	+	-		1.9	8.4	4.0	53
25	+			1.3	9.0	4.7	48
26	+			3.1	16.9	9.4	44
27	+			2.6	15.1	7.3	52
28	+			2.3	17.4	11.4	35
29	+			0.7	13.8	10.8	22
30	+	+		1.4	7.1	4.6	35
31	+			1.5	15.7	10.9	30
32	+			2.7	19.0	13.9	27
33	+	+	+	0.7	7.2	4.5	38
34	+			1.4	12.3	8.2	33
35	+			1.5	21.3	15.4	28
36	+			1.5	14.2	9.3	35
37	+	+		3.3	9.4	8.6	7.9
38	+	+		0.7	18.1	15.8	13
39	+	+		7.0	18.3	4.7	74
40	+	-		7.4	27.2	10.4	62
41	+			2.7	23.9	12.7	47
42	+	+		2.1	5.7	4.4	23
43	+	+		1.5	6.5	5.0	22
44	+	-		7.1	26.3	10.1	62
45	+			0.3	5.8	3.7	36
BW 3				9.1			
BW 4				2.3			

samples, it is important to note that all 45 papers were not very sensitive to light exposure, and would be judged to have lightfastness ratings better than Blue Wool 3. Similar results were reported in a previous study (Altherr 1965; Wilhelm 2003). Materials with

degradation rates less than Blue Wool 3 are considered to have at least intermediate light-sensitivity and are expected to have a useful lifespan of at least 20–100 years in an indoor daylit environment (Feller 2002).

## OPTICAL BRIGHTENERS IN BLACK-AND-WHITE PHOTOGRAPHIC PAPER: APPEARANCE AND DEGRADATION

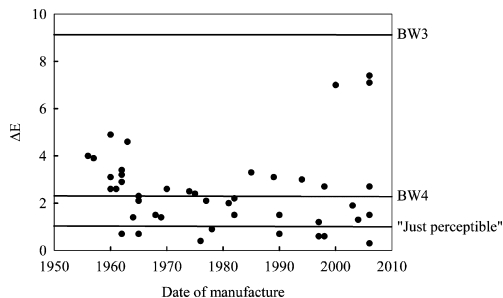


Fig. 6. Overall color difference ( $\Delta E^*$ ) after 6.5 Mlux-hrs light exposure for all paper samples as a function of date of manufacture. The three solid lines indicate the just perceptible  $\Delta E^* = 1.0$ , the ISO Blue Wool 3  $\Delta E^* = 9.1$ , and the ISO Blue Wool 4  $\Delta E^* = 2.3$ , with the same light exposure.

### 4.3 OPTICAL BRIGHTENER LOSS

While the color difference,  $\Delta E^*$ , describes the overall color change due to optical brightener loss, bleaching/yellowing of the substrate, and fading of the chromophore at 570 nm, the peak at 430 nm when UV is included in the measurement is due exclusively to the optical brightener. The loss of optical brightener can thus be tracked separately by following the changes in the intensity of the spectral peak at 430 nm. The initial amount of optical brightener was calculated to be the difference in percent reflectance,  $\Delta R_{430}$  (initial), in the spectra measured with UV included versus UV excluded before light exposure. The final amount of optical brightener,  $\Delta R_{430}$  (final), was calculated from the difference between the same two spectra (UV included versus UV excluded) after 6.5 Mlux-hrs of light exposure. The % optical brightener loss (%OBA loss) is calculated as

$$\% \text{ OBA loss} = \frac{\Delta R_{430}(\text{initial}) - \Delta R_{430}(\text{final})}{\Delta R_{430}(\text{initial})} \times 100\% \quad (1)$$

The results are listed in table 3.

The forty-five samples had a % OBA loss ranging from 7.9 (Sample 37) to 88 (Sample 14), with an average of 49. However, the average % OBA loss for only Kodak samples, (Samples 1–25) at  $59 \pm 10$ , is slightly greater than the  $31 \pm 11$  average % OBA loss for the other samples, excluding the three samples 39, 40, and 44 which showed a significant color change (see section 4.2). Results of a *t*-test with a 95% confidence level show that the two populations, Kodak versus other papers, are statistically different. Further, pho-

tographic papers that initially had large color changes from optical brightener activation ( $\Delta E^* > 5.8$ , listed in table 2) had an average % OBA loss of 39, showing these samples have no greater propensity to optical brightener loss from light exposure than any of the other samples. In fact, after 6.5 Mlux-hrs of light exposure, optical brightener is still present in all the samples (even samples 39, 40, and 44, which had the largest  $\Delta E^*$ ) after aging.

### 5. CONCLUSIONS

This study determined the impact that optical brighteners have on a paper's appearance, the overall color changes that result from prolonged light exposure, and the light-sensitivity of the brighteners themselves. The activation of optical brighteners in black-and-white photographic paper by inclusion of UV radiation in the illuminating light source affects the appearance of the paper to varying degrees. The papers studied were usually relatively white in their unbrightened state and changed in appearance to slightly more white or very blue-white upon activation of their optical brightener. The appearance change experienced by one-third of the papers was larger than the rest, and exclusion of UV radiation from the illuminating light source for these papers may cause a noticeable change in the papers' appearance. The contribution from fluorescent emission to the appearance of the photographic papers studied varied from one manufacturer to another. Kodak papers regularly showed a smaller contribution from fluorescent emission compared to either Ilford or Agfa papers and therefore may not gain enough brightened appearance change to warrant inclusion of UV wavelengths in the illumination.

The overall color change due to accelerated light aging with UV radiation included was attributed to optical brightener loss, bleaching or yellowing of the paper substrate, and fading of a chromophore at 570 nm. In 8 of the 45 samples, color change was below a perceptible limit; in the other 37 samples, it was above this limit. The Kodak samples manufactured before 1964 tended to be more light-sensitive than many of the other papers. Three papers, made by Ilford and Oriental, experienced the greatest color change, indicating that a component in these samples is more light-sensitive than in papers used by other manufacturers. However, the degradation rate for all photographic papers studied was less than that of Blue

SANDRA A. CONNORS-ROWE, PAUL M. WHITMORE,  
AND HANNAH R. MORRIS

Wool 3, and therefore they should be considered moderately light-sensitive materials.

Although there were a variety of light-sensitive components to the photographic papers, all the samples experienced a decrease in fluorescent emission due to loss of optical brightener, losing on average 49% of the original brightener fluorescence. However, the 25 Kodak papers analyzed had an average of 59% optical brightener loss. Therefore, the Kodak papers, which had smaller appearance changes from inclusion of the optical brightener, also seemed to have an optical brightener that was more sensitive to light exposure. However, these papers did not show the greatest overall color change, which included all three types of color change and not just the optical brightener loss.

The exposure of these tested papers to illumination containing UV, necessary to achieve the optically brightened appearance, caused only small changes in overall color. Therefore, inclusion of UV in museum lighting may be considered if the optically brightened appearance of the photograph is important to its interpretation, a decision that can only be made through discussions between all those responsible for a given photograph's care and exhibition. However, inclusion of UV should only be considered when it will make a significant change to the appearance of the paper, which occurred in only one third of the papers studied. Although Ilford and Oriental papers had faster degradation rates versus those of Kodak papers, the trend for all the papers showed they were not very sensitive to light, with lightfastness greater than Blue Wool 3 or 4. Of course, exposure to UV radiation should only be considered if no other part of the photograph will be adversely affected by UV exposure.

Further study is necessary to confirm trends in optical brightener usage in various brands of paper from a single manufacturer and to see if all Ilford and Oriental photographic papers follow the trend indicated here. Further study is also warranted to explore variations in brightener performance and stability from different photograph processing methods and to determine appropriate UV wavelengths to include in exhibition lighting conditions.

## APPENDIX: EXPERIMENTAL

Forty-five black-and-white photographic paper samples were chosen from the collection assembled by Paul Messier, of Paul Messier LLC, Conservation of

Photographs, Works on Paper and Electronic Media. All papers provided had been prepared through the following procedure. The papers originated in sealed manufacturer's packaging. The packages were opened in a photographic darkroom under safe light. A single sheet of paper was removed and a 2 × 2 in. piece of paper was cut from the sheet. The remaining paper was returned to the package and the package was resealed. Each sample was fixed using ammonium thiosulfate, washed in water for 25 minutes, and air-dried.

The papers chosen for study thus came from sealed packages of photographic paper with definite manufacturer, brand, and date information. The papers chosen also exhibited blue-white fluorescence on the recto of the paper when viewed under black light and did not exhibit contamination from other brightened papers (i.e., through transfer of the water-soluble brightener during paper processing). The presence of optical brightener in the chosen papers was confirmed through spectroscopic measurements.

Fluorescent excitation and emission spectra were collected using a Fluorolog ISA fluorimeter (Jobin Yvon, Horiba Group) in order to confirm the presence of optical brightener in the paper samples. Extracts of the optical brightener were prepared by placing a 0.05 g sample of each paper, cut into small pieces, into 20 ml of HPLC grade water and acetonitrile (65:35 by volume). Each sample was shaken for 24 hours before analysis. The extract from each sample was placed in a quartz fluorescence cuvette for analysis. Excitation spectra were collected between 200–400 nm with an emission wavelength of 430 nm, integration time of 0.5 s, and an increment of 1.0 nm. Emission spectra were collected between 375–575 nm with an excitation wavelength of 350 nm, integration time of 0.5 s, and an increment of 1.0 nm. Comparison was made between the excitation and emission spectra of the paper extracts and solutions of two reference optical brighteners known to be used in the photographic paper industry, Tinopal SFP and Leucophor BCF 115. These reference brighteners are made with derivatives of the stilbene molecule, a chemical thought to be widely used to brighten photographic papers. Excitation and emission spectra were also collected from the paper samples directly, using the Fluorolog ISA fluorimeter. Each paper sample was placed at a 30° angle to the incident light path and the fluorescence emission was collected at an angle of 60°. Excitation spectra were collected between 200–425 nm while detecting at an emission wavelength of 435 nm, integration time of 0.5 s, slit width of 0.8 nm,

## OPTICAL BRIGHTENERS IN BLACK-AND-WHITE PHOTOGRAPHIC PAPER: APPEARANCE AND DEGRADATION

and an increment of 1.0 nm. Emission spectra were collected between 385–575 nm with an excitation wavelength of 375 nm, integration time of 0.5 s, slit width of 0.8 nm, and an increment of 1.0 nm.

Initial color measurements were made for all paper samples using a GretagMacbeth Color Eye 7000 Colorimeter equipped with a xenon lamp. Two reflectance measurements (specular reflectance excluded) were made for each sample: (1) with UV excluded from the illuminating light source using the instrument's UV filter (390 nm cutoff) which was placed in the optical path, and (2) with UV included in the illuminating light source by removing the UV filter. The measurement with UV excluded from the light source estimates that paper's appearance due to reflected light alone (i.e., with the brightener not activated) and the measurement with UV included in the light source shows that paper's appearance with both reflected and emitted light present (i.e., with the brightener activated). A single measurement was taken for each sample and was considered to be representative of the whole. The reproducibility of the Color Eye 7000 intensity measurement at 430 nm (optical brightener peak maximum) was  $\leq 0.1\%$ R when samples were removed from the instrument for light aging and then positioned back to the same location on the sample. ProPalette version 5.2 software for this instrument provided reflectance data as well as tristimulus values calculated for  $10^\circ$  observer and standard illuminant D65. Yellowness Index values were calculated using the method described in ASTM standard E313-73 (1993) and using standard illuminant D65. The Yellowness Index value of a barium sulfate ( $\text{BaSO}_4$ ) reflectance standard was used for comparison. This reference material was chosen because of the frequent use of barium sulfate in the baryta layer of black-and-white photographic paper.

All paper samples were exposed to high-output daylight fluorescent lamps (General Electric F48T12-D-HO) with UV radiation included in the exposure. The light intensity used to achieve the results discussed in this study was  $1.02 \times 10^4$  lux, as measured by a radiometer in lux for a diffuse light source (International Light IL1700 with detector SED010 351, filter Y 70 and diffuser W 323). The total UV content of the lamp output was measured to be  $6.18 \times 10^{-5}$  W/cm<sup>2</sup> or 2.3% of the total lamp output (International Light IL1700 with detector SED400 383, filter 20162, diffuser 313, and set to 5V bias). Samples were kept at 23°C and 50% relative humidity throughout the fading experiment. All paper samples were also

exposed to higher light intensity ( $3.43 \times 10^4$  lux) exposure conditions to determine if reciprocity failure was a problem at higher light levels. No problem with reciprocity failure was found.

Color measurements were made throughout the exposure to accelerated light-aging conditions, a total of eleven measurements, using a GretagMacbeth Color Eye 7000 Colorimeter. Reflectance data were collected for each sample with UV included and with UV excluded from the illuminating light source, as described above. Overall color differences from light exposure were calculated with the 1976 CIE L\*a\*b\* formula for  $\Delta E^*$ .

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SANDRA A. CONNORS-ROWE, PAUL M. WHITMORE,  
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www.cibasc.com (accessed 2005).

## SOURCES OF MATERIALS

Black-and-white photographic papers  
Paul Messier, LLC, Conservation of Works on Paper, Photographs and Electronic Media  
103 Brooks St.  
Brighton, Mass. 02135  
(617) 782-7110

Tinopal SFP, optical brightener  
Ciba Specialty Chemicals, Inc.  
205 South James St.  
Newport, Del. 19804  
(800) 355-2422

Leucophor BCF 115, optical brightener  
Clariant Corporation  
4000 Monroe Rd.  
Charlotte, N.C. 28205

Water, HPLC grade  
Fisher Scientific (cat. no. W5-1)  
4500 Turnberry Dr.  
Hanover Park, Ill. 60133  
(800) 766-7000  
www.fishersci.com

Acetonitrile, HPLC grade  
Fisher Scientific (cat. no. A998-1)  
4500 Turnberry Dr.  
Hanover Park, Ill. 60133  
(800) 766-7000  
www.fishersci.com

## OPTICAL BRIGHTENERS IN BLACK-AND-WHITE PHOTOGRAPHIC PAPER: APPEARANCE AND DEGRADATION

Colorimeter (Color Eye 7000)  
GretagMacbeth  
617 Little Britain Rd.  
New Windsor, N.Y. 12553  
(845) 565-7600

Fluorescence spectrometer (Fluorolog ISA)  
Jobin Yvon Inc.  
Horiba Group  
3880 Park Ave.  
Edison, N.J. 08820  
(732) 494-8660  
www.jyhoriba.com

High-output daylight fluorescent lights (General  
Electric model F48T12-D-HO)  
Grainger, Inc.  
3150 Liberty Ave.  
Pittsburgh, Pa. 15201  
(412) 281-4477  
www.grainger.com

Radiometer (model IL1700)  
International Light, Inc.  
17 Graf Rd.  
Newburyport, Mass. 01950  
(978) 465-5923  
www.intl-light.com

Bottle shaker  
Burrell Scientific, Inc.  
2223 Fifth Ave.  
Pittsburgh, Pa. 15219  
(412) 471-2527

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