Influence of UVA Spectral Absorption and Photopermanence on the Weatherability of Laminated Ink Jet Graphics

Joseph C. Suhadolnik, Andrea Smith, Nancy Cliff, Harry J. Evers III,*
Mervin Wood, Michael Amone, and Walter Renz
Ciba Specialty Chemicals Corporation
Tarrytown, New York

Abstract

Unprotected ink jet graphics fade when exposed to natural or artificial light. Protective laminates containing ultraviolet absorbers (UVAs) are commonly applied over printed surfaces intended for exterior use to slow degradation caused by the ultraviolet component of sunlight. While this affords a level of UV protection, little has been reported about the influence of UVA chemistry on the longevity of coated / laminated prints. This is of relevance because UVAs differ both in their ability to screen specific portions of the UV spectrum and their photopermanence in various media which can limit their efficacy over time.

Commercial and experimental UVAs (benzophenones, benzotriazoles, triazines) were incorporated into two different protective coatings which were applied over test prints made using commercial narrow- and wide-format ink jet media / inks and weathered under dry xenon conditions. This paper describes the significant differences in color loss of both dye and pigment-based ink sets that result from the differences in spectral absorption and photopermanence of the various UVAs. The best results were obtained using novel photostable UVAs having broad absorption profiles across the long-wavelength UV region.

Introduction

Laminates and clear top coats can be used to protect ink jet images from fading caused by environmental factors such as moisture, pollutants and UV light.[1] Laminates are most widely used in outdoor applications where the image is exposed to weather and direct sunlight but may also have value indoors where fading caused by indirect sunlight, artificial light, and airborne pollutants is still encountered. Dye-based images are generally more sensitive to the effects of light and moisture than pigment-based systems; however, the combined effects of light and oxygen can cause premature fade of even pigment-based prints. Protective laminates therefore routinely incorporate UVAs to screen the underlying image from the harmful effects of UV light.

In choosing a UVA, the most obvious factors that need to be considered are its absorption profile and durability. Other important properties include substrate compatibility and volatility. UVAs are now available with improved photopermanence and red-shifted absorptions approaching the onset of visible light at 400 nm. Determining which wavelengths of UV light are most responsible for color loss would indicate whether these red-shifted compounds provide added value.

Although dyes and pigments strongly absorb light in the visible region, screening UV light can have a significant effect on color permanence. Many dyes are known to be more sensitive to some wavelengths of light than others.[2] Even the UV screening provided by window glass will improve the photo-fastness of some systems.[3] New red-shifted UVAs are finding use in window film applications where their ability to block a broader segment of the UV spectrum slows the fade of colored articles within a room, such as fabrics and pictures.[4] In the present case of laminated prints, there is the additional benefit of reducing the impact of oxygen and airborne pollutants. The stability of the UVA plays an important role in maintaining the integrity of the laminate, especially for more stable pigmented systems.

Recent work has examined the specific wavelengths responsible for dye photodegradation, i.e., the activation spectra.[5] Not surprisingly, different dyes, and even the same dyes in different media, have different sensitivities to various wavelengths of light. Given that a variety of dyes, pigments and media are commercially employed, a universal statement on the effectiveness of UVAs is impossible. We can explore the practical application of the wavelength dependency of color fade by examining the effect of various classes of UVAs in light absorbing laminates over printed images.

For less photopermanent dye-based images, the UVA absorption profile may be more important than its durability as color change may become noticeable before the loss of UVA becomes an issue. However, relatively unstable UVAs may require higher load levels to compensate for absorption lost due to stabilizer degradation. For more photopermanent systems, such as pigment based images, the durability of the UVA increases in importance.

This paper describes the relative effectiveness of different UVAs in laminates over ink jet images to determine whether absorption profile or photo-permanence plays an appreciable role in preventing observed color loss. It is not our intention to predict the lifetime of print systems or to compare competing print systems with one another.

Experimental

Test patterns consisting of single-colored one inch square blocks of cyan, magenta, yellow, and optionally black (100% print density) were printed on commercially available media using commercially available dye or pigment based ink sets. The prints were dried for 24 hours and coated with model coating formulations containing the trial UVAs at concentrations of between 2-3 % based on resin solids, both with and without 3 % of the hindered amine TINUVIN® 123. UVA concentrations were chosen to provide similar UV absorbances near UVA λ max. A number of prints were also either not coated or coated with unstabilized coatings.

Preparation of Coated Samples

Dye-Based Prints - Test patterns of cyan, magenta, and yellow printed on glossy photo paper using a HP 970 printer, and similar patterns of cyan, magenta, yellow, and black printed on photo glossy wide format paper using an ENCAD NOVAJET® 700 wide format printer were coated with acrylic coating formulations based on SURCOL® 836 using a calibrated draw down bar (Number 4 K-bar) yielding approximately 10 gsm coating density on the prints.

Pigmented Prints - Patterns of cyan, magenta, yellow, and black were printed on photo glossy wide format paper and matte vinyl media using an ENCAD NOVAJET® 700 wide format printer and pigment-based inks. These were coated with a model UV-cured formulation based on a commercial acrylated urethane and TMPTA using a wire wound rod to give a 4 mil wet coat.

Exposures

The samples were exposed, without window glass, in an Atlas Ci65 Xenon Arc Weatherometer, 0.35 W/m^2 irradiance at 340 nm, using both inner and outer borosilicate Type S filters at 50^{o}C, 50% humidity, no water spray or light / dark cycle. CIE L*a*b* color and optical density, were monitored (X-RITE Spectrodensitometer) at ~24 hour intervals over 200 hours for the dye based images, and at 100-250 hour intervals (1000 hours to date) for the pigmented images.

Color loss is presented as a loss in optical density (OD) as it correlated reasonably well with visible observations.

Results and Discussion

Figure 1 shows the structures of the UVAs selected for study: benzophenones CHIMASSORB® 81 (Bp 1) and red-shifted derivative (Bp 2), benzotriazoles TINUVUN® 928 (Bzt 1) and red-shifted CGL 139 (Bzt 2), triazines TINUVIN® 400 (Tz 1) and experimental red-shifted triazine (Tz 2). The transmission spectra show the absorption cutoffs of the various UVAs, 70 mg/L in ethyl acetate, Figure 2.

The photopermanence of UVAs in polymers and coatings has been widely investigated.[6,7] While the results can be matrix dependent, benzophenone UVAs are generally less stable than benzotriazoles or triazines. Triazine UVAs are often more stable than benzotriazoles, but this can be affected by substituents; Bzt 1 is very stable in comparison to other benzotriazoles and Bzt 2 is at least as durable as triazines in many applications,[8] Figure 3.

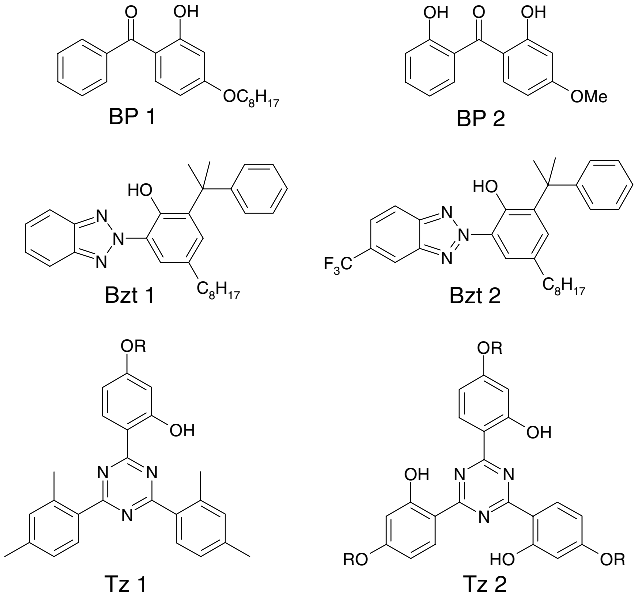

Figure 1. Structures of test UVAs

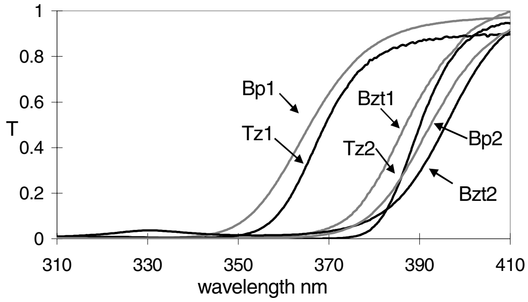

Figure 2. Transmission spectra of UVAs at 70 mg/L in EtOAc

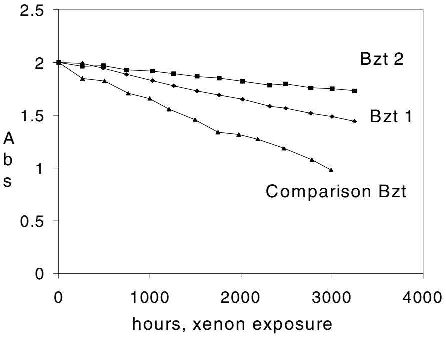

Figure 3. Loss of UVA absorption at λ max over time for Bzt 2 and Bzt 1 vs. a less stable benzotriazole in an automotive coating.

Fade of Dye Based Prints

Under the exposure conditions, similar to outdoor sunlight, incorporation of UVA into the acrylic top coat had a positive effect on both the HP 970 glossy photo prints and the wide format prints. Bp 2 was not screened in this case due to unacceptable yellowing. The response of each dye to the different UVAs is detailed below. The following tables represent formulations without HALS.

HP 970 Prints

Yellow - Very little yellow fade from the HP 970 generated prints was seen after 200 hours of exposure. Less than 15 % of initial color density (OD, 0 hr) was lost from any sample including those with unstabilized laminates.

Cyan - More fade was observed from these cyan prints, with fade in the early portion of the exposure more rapid than later on, see Table 1. Initial OD for the 3 starred (experimental Bzt 3 is similar in structure and UV spectra to Bzt 2) formulations were higher making a direct comparison difficult. The data still clearly show that benzotriazoles and triazines modestly improve dye fade.

Table 1. Loss of cyan dye OD from photo paper.

UVA*	OD	Loss of OD / time		
	0 hr	48 hr	100 hr	200 hr
none	1.01	**0.32** 32%	**0.37** 37%	**0.45** 45%
Bp1	1.01	**0.32** 32%	**0.40** 40%	**0.47** 47%
Btz1	1.01	**0.23** **23%**	**0.27** 27%	**0.33** 33%
Btz 2	1.02	**0.24** 24%	**0.29** 29%	**0.35** 35%
Tz 1*	1.52	**0.47** 30%	**0.55** 36%	**0.61** 40%
Tz 2*	1.52	**0.40** 26%	**0.48** 32%	**0.58** 38%
Bzt 3*	1.52	**0.35** 23%	**0.40** 26%	**0.43** 28%

The slight advantage seen for the benzotriazoles, and the lack of effectiveness of Bp 1 may indicate some sensitivity of this ink to longer wavelength UV light.

Magenta - As in the preceding example, differences in initial OD preclude a direct comparison of all the data, Table 2. Nonetheless, it is obvious that the benzotriazoles are quite effective in slowing the significant fade of the magenta, the triazines less so, compare Tz 1 and Tz 2 vs. Bzt 3, while the benzophenone offered no improvement. In the earlier time intervals, red-shifted Tz 2 appears to have an advantage over Tz 1. The decrease in the performance of Tz 2 over time may be a result of UVA loss from the aged coating as the formulation containing both Tz 2 and HALS maintained its performance level. Together with the strong performance of Bzt 1, Bzt 2, and Bzt 3, this suggests an advantage in screening the longer wavelength UV.

Table 2. Loss of magenta dye OD from photo paper

	OD	Loss of OD / Time		
UVA	0hr	48	100hr	200hr
none	2.54	**0.57** 22%	**1.32** 52%	**2.28** 90%
BP 1	2.59	**0.80** 30%	**1.50** 58%	**2.36** 91%
Btz 1	2.62	**0.28** 11%	**0.55** 21%	**1.29** 49%
Bzt 2	2.65	**0.31** 12%	**0.60** 22%	**1.32** 50%
Tz 1*	1.49	**0.14** 9%	**0.60** 40%	**1.13** 76%
Tz 2*	1.49	**0.05** 3%	**0.48** 32%	**1.31** 88%
Bzt 3*	1.47	**0.17** 12%	**0.37** 25%	**0.95** 65%

Wide Format Dye-Based Prints

Yellow - The wide format dye-based prints exhibited complete loss of yellow color during exposure. UVAs in the top coat were able to slow fade in the early hours of exposure, with the more red-shifted compounds, Bzt 1, Bzt 2, and to a small extent Tz 2, having a larger impact than the others, Table 3.

Cyan - There was only modest fade for the cyan, ~ 25% OD loss after 200 hours for the sample with no added UVA. Either of the two triazines cut this loss in half, but Bp 1 and either benzotriazole reduced fade even more. In this case, it appears that screening the short wavelength UV is as effective as screening the longer wavelengths, Table 4.

Magenta - As before, Bzt1 and Bzt 2 were quite effective in slowing the substantial fade of magenta, Table 5. The decline in the modest early activity of Bp 1 is probably due to poor photostability in this matrix. The presence of HALS did not improve the performance of BP 1. While the optical density loss in Table 5 is similar for both benzotriazoles tested, visual inspection of the samples clearly show the advantage of the more red-shifted Bzt 2.

Table 3. Loss of yellow dye OD from wide format paper

	OD	Loss of OD / Time		
UVA	0 hr	24 hr	48 hr	72 hr
none	1.54	0.47	0.88	1.09
Bp 1	1.54	0.31	0.71	0.96
Btz 1	1.56	0.17	0.58	0.79
Btz 2	1.55	0.22	0.59	0.89
Tz 1	1.55	0.35	0.75	1.04
Tz 2	1.56	0.33	0.67	0.98

Table 4. Loss of cyan dye OD from wide format paper

	OD	Loss of OD / Time	
UVA	O hr	100 hr	200 hr
none	2.65	0.39	0.67
Bp 1	2.66	0.19	0.25
Btz 2	2.68	0.17	0.24
Tz 2	2.74	0.28	0.33

Table 5. Loss of magenta dye from wide format paper

	OD	Loss of OD / Time		
UVA	0 hr	48	100hr	200hr
none	2.67	1.49	2.29	-
Bp 1	2.63	0.51	1.25	2.36
Btz1	2.65	0.33	0.62	1.56
Btz 2	2.59	0.35	0.86	1.61
Tz 1	2.62	0.64	1.37	2.13
Tz 2	2.69	0.63	1.43	2.07

Given the difference in UV absorption cutoff between Tz 1 and Tz 2, it is curious that both offered only modest improvement relative to the benzotriazoles. This may be due to differential UVA migration into the image layer or matrix incompatibility, however, a more intriguing explanation may be found in the absorption profiles of these compounds.

While triazine UVAs have extremely high extinction coefficients, Tz 1 has a deficiency in the longer wavelengths whereas Tz 2 absorbs less between 290 - 330 nm, Figure 4.

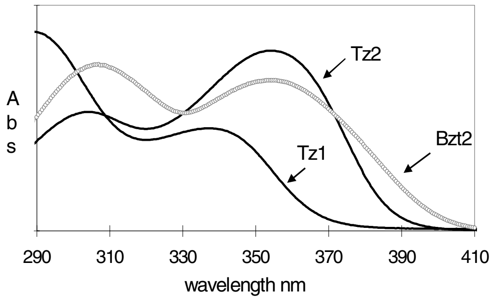

Figure 4. Normalized UV absorption of Tz1, Tz 2 and Bzt 2.

The early effectiveness of Bp 1 and the good performance of Bzt 1 and Bzt 2 indicates a sensitivity to both near and far regions of terrestrial UV. The broad even coverage of Bzt 1and Bzt 2 throughout the UV spectrum may be responsible for their enhanced activity. Enhancing the far UV absorbance of Tz 2, or using Tz 2 behind window glass could offer the same improved protection.

The benzotriazoles used here provided the best overall dye protection through a combination of photo-permanence and a broad, evenly distributed absorption. The triazine UVAs also performed well. Bp 1 performed poorly, either as a result of a narrow absorption profile or poor stability. It is interesting that the wide format cyan was equally improved by any of the UVAs tested, while the cyan from the HP 970 prints responded more favorably to the red-shifted compounds. The strong response of the magentas in this study to the red-shifted compounds suggests that the long wavelength UV found in indoor lighting causes significant dye loss.

Pigmented Systems

After 1000 hours of xenon exposure, all of the laminated prints retain excellent color. The unlaminated vinyl has lost 50% of cyan and magenta, the unlaminated paper print lost all color. The laminates containing UVAs are outperforming those without UVA but it is too early to differentiate between the UVAs, and exposures continue.

Conclusion

The choice of UVA has a large impact on the effectiveness of UV screening laminates in slowing photo fade of dye or pigment based images. While in some dye systems, e.g. the wide format cyan in this study, degradation is due mainly to short wavelength UV; other dyes, such as magenta, are affected by both the short and long wavelengths. This sensitivity to long wavelength UV suggests a benefit for light absorbing laminates even in demanding indoor applications. Durable, broadly absorbing, red-shifted UVAs such as Bzt 2 provide the best protection.

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Biography

Joseph Suhadolnik is Senior Staff Scientist in the Research department of Ciba Specialty Chemicals in Tarrytown, New York. Principal areas of research include the photochemistry of light stabilizers and photo-decomposition of dyes and pigments. He holds several patents on novel light stabilizers and has published papers on the degradation mechanisms of UVAs. He received a B.A. in chemistry from the University of Pennsylvania in 1980 and Ph.D. in organic chemistry from the University of Minnesota in 1985.