Development of Image Longevity Enhancing UV Blocking PET Overlamination Films

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Abstract

Printed graphics are susceptible to the degratory effects of UV light, rain, ozone, pollution and other external stimulus. In particular, the constant exposure of printed graphics to bright light sources is known to cause serious degradation to the color vibrancy and expected lifetime of the medium. Previously, overlamination has been used with some success to improve the longevity of inkjet printed graphics.[1] However, sacrifices to clarity, surface quality, tensile strength and color of the overlamination films were made in this pursuit. We describe a novel overlamination base constructed from new weatherable PET technology that affords many useful advantages compared to older technologies.

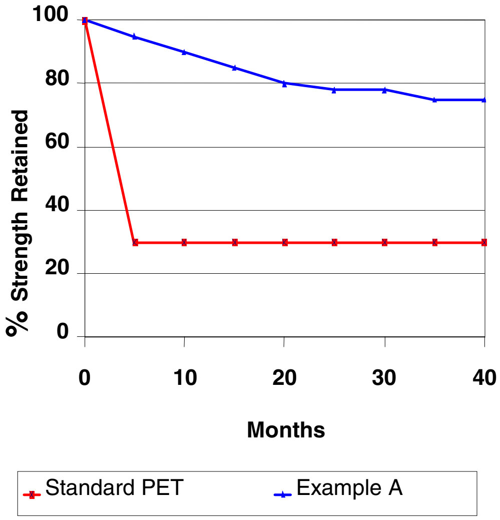

Figure 1. EMMAQUA® (Equatorial Mount with Mirrors for Acceleration with Water) testing for PET films. It is the most widely used outdoor accelerated weathering test method, provided by Atlas Weathering Services Group.

Introduction

Polyethyleneterephtlate (PET) is an abundant man-made material, often commonly referred to as polyester. This engineering plastic is well known for clarity, high modulus and dimensional stability under aggressive thermal loads. Unfortunately, polyester films suffer from very poor stability to the degratory effects of solar radiation. Chain scission mechanisms[2-3] are very rapid in polyester films, helped, mainly, by the high molar extinction coefficient of the benzanoid structure of the polyester chain backbone. Shown in Figure 1 is an example of the physical degradation of PET film as measured by the retention of load at break.

The clarity, web-handling efficiency, strength, surface properties and environmental friendliness of PET make polyester films an excellent material for overlamination use for many substrates. However, the lack of weatherability of the material limits the use to relatively short-term outdoor uses and indoor applications. Therefore, it would be desirable to modify the polyester film to improve the weatherability of the material without degrading the other beneficial features of the material. Also, importantly, the facilitation of UV screening of the base film was determined to improve the image longevity of inkjet prints.

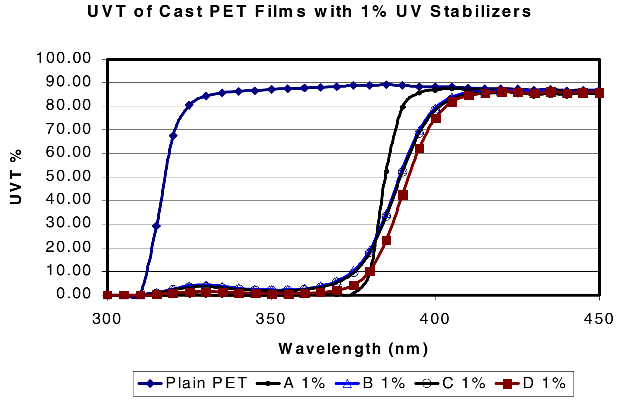

Figure 2. Spectral transmittance curves for PET films, compounded with various, thermally stable, UVAs. The goal for our development was to absorb as much from the UV spectrum without resulting in a yellow film.

Experimental

Polyester film was UV compounded as follows:

Specific UV stabilizing materials, UVAs, here for simplicity, labeled as A, B, C, and D, ca. 20% by weight, were admixed into PET chip with an intrinsic viscosity (IV) of 0.65, into a co-rotating twin screw extruder. The extruded strands were cooled in a water trough and pelletized via cutting on a rotary cutting line. The resultant pellets were then admixed with pure 0.65 IV PET chip and extruded onto a casting drum to produce a PET sheet of about 1.0mil thickness. Film was prepared at 0.5%, 1%, and 3% by weight of UV stabilized PET sheet. No discoloration of the 1 mil cast film was observed.

The UVA properties of the polyester films were measured via the use of a Hitachi U-3210 UV/VIS spectrophotometer. UV transmission spectra were taken and the percentage of total UV transmittance was calculated from 300nm to 400 nm as an area percent. Therefore, 0 area % would indicate complete cutoff in the range of 300nm to 400nm. All the related UV-Vis transmission spectra are plotted in Figures 2 and 3.

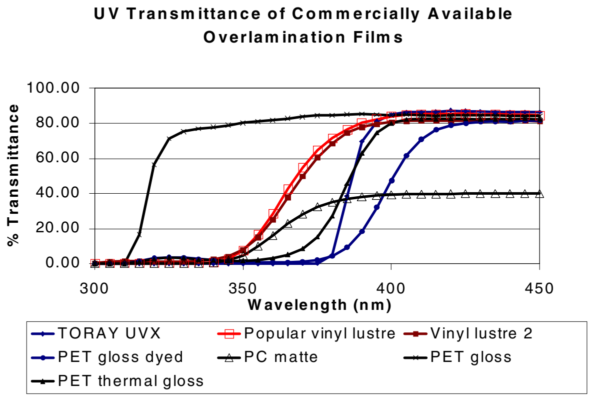

Figure 3. Spectral transmittance curves of commercially available overlamination films. The technology described here has the lowest UV transmittance without any transmittance loss in the visible range (i.e. water white).

The test overlamination films were then prepared via handcoating the PET sheets with a light tack acrylic laminating adhesive. These adhesive coated films were then hand laminated against inkjet printed graphics to determine the efficacy of the improvement of the durability of the images.

Description of Test Laminate

The film samples as described above were overcoated with a light tack acrylic adhesive (National Starch 30-9172) using a #5 Meyer rod and were dried in a forced convection oven at 125°C for about 10 seconds. The adhesive coated sheets were then placed onto test image samples prepared with an Epson Stylus 9000® inkjet printer utilizing Epson dye based inkjet inks and laminated with constant hand pressure. The test images consisted of cyan (C), magenta (M), yellow (Y), red (100% yellow, 100% magenta), blue (100% cyan, 100% yellow), green (100% cyan, 100% magenta) and pure black (K) image areas. The image CIELAB D65 values of the laminated images were measured using a Xrite SP62 spectrophotometer before exposure to UV light in the Atlas weatherometer. The laminated samples were then placed in an Atlas C35A weatherometer, maintained at about 35°C chamber temperature and exposed to high pressure Xenon light at a pressure of 0.45 W/m^2.nm for a variable time. The CIELAB D65 colorimetery values for the exposed samples were then measured and a total fading amount (ΔE) of five colors (RGCMY) after t hours was calculated according to the following equation:

$$\Delta E_t = \Sigma(RGCMY)\{(L_0-L_t)^2 + (a_0-a_t)^2 + (b_0-b_t)^2\}^{0.5} \qquad (1)$$

Results and Discussion

Total fade data of inkjet images protected by UV stabilized PET film using different UV stabilizers after variable exposure time to high pressure Xenon-arc light in the Atlas weatherometer are listed in Figure 4.[4]

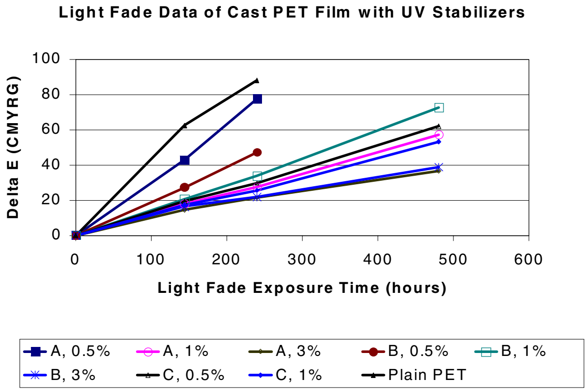

Figure 4. Lightfade of inkjet printed samples overlaminated with novel, weatherable, PET films.

For the purposes of this discussion the level of Total Fade as a function of time deemed acceptable is 40 units or less.[5] As can be readily seen from the data in Figure 4, the UV stabilized film results in laminated images with significantly longer lifetime under exposure to degratory UV light sources than plain PET film, without resulting in yellowing of the background coloration.

Due to the overall good performance and the processabilty, UVA type C was further developed. A 1 mil biaxially oriented film, which contains ~1% by weight of C was prepared on a commercial PET film line. This weatherable PET film was then coated with acrylic pressure sensitive adhesive applied at ~22 or 27g/m^2 coating weight on a 74” wet bond laminator PSA coater. A 142G PET was used for the release liner. This film was then laminated to a test plot as described for testing in the Atlas Weatherometer by utilizing a Ledco PSA type laminator. The technology described here is referred to as uvX™.

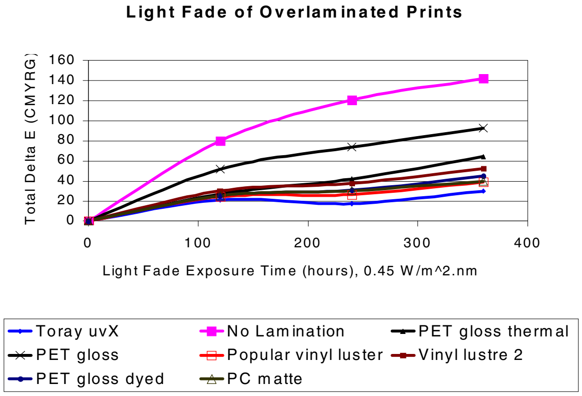

Figure 5. Analysis of lightfade enhancement of overlaminate films and inkjet prints. The film technology described here, called uvX™ films, gives the largest image enhancement.

For comparison, various of commercially available overlamination films were also tested in the Atlas weatherometer at the same time. Figure 5 shows the total lightfade as a function of exposure time. The results show that uvX™ film is the best in preserving the original color. Furthermore, analysis of individual color fade show (Figure 6) that uvX™ is the best to prevent catalytic fade so that there is no or minimum color shift occurs during the lifetime of the prints. This implies that there is a reduced possibility of obnoxious color shifts for media overlaminated with the film technology described here.

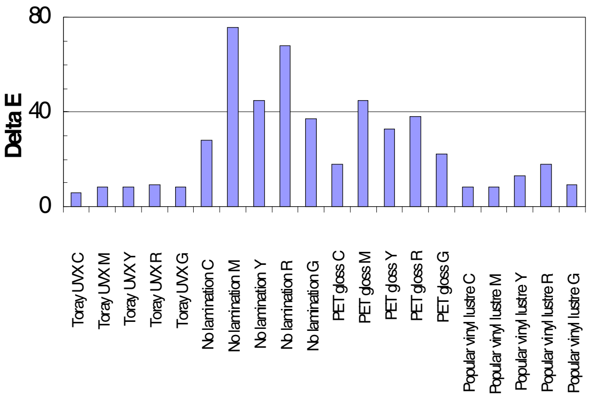

Figure 6. Deconvolution of total color fade, into individual color fade, shows that fade is consistent for each color when overlaminated with uvX™ materials.

We have also laminated uvX™ to a major OEM pigment base ink. Although the results showed that the lightfade was much less with time, it still showed sign of fade. uvX™ lamination film, again, showed the improvement over no lamination (Figure 7). Furthermore, it was apparent that from the lightfade data that using different media, light fade varies. However, with uvX™ lamination, the total light fade is consistent and predictable.

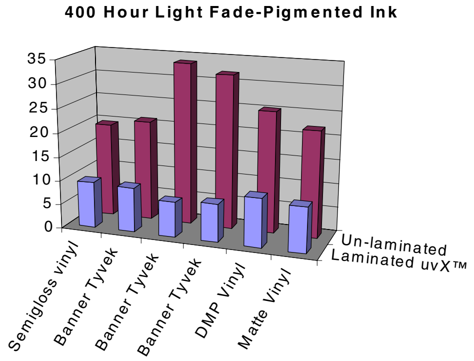

Figure 7. 400 hours lightfade of a pigment ink at different outdoor media.

When a UV absorber preferentially absorbs the UV light, it forms intermediate molecular structures with higher energy. They reversibly return to their original form by dissipating the energy as harmless heat through the polymer matrix. Therefore, UV absorbers can not only protect the plastic materials from degradation, but also prevent the harmful UV from reaching the items behind the plastics.

The reasons behind the excellent performance of uvX™ overlamination lie in the rigidity of PET film as well as the high performance UV absorbers used to make UV film. Typical UV stabilizers are low molecular weight organic moieties. When admixed into a relatively rigid PET matrix the UV stabilizers are, therefore, surrounded by a constraining material. If the UV absorbers undergo covalent bond breakage via the conversion of light energy, the resultant free radical structures produced are locked into a relatively rigid cage. This then enhances the longevity of the UVAs by facilitating the recombination of the free radical pairs back into covalently bonded materials before facile bond re-arrangement can take place.[2-3]

The glass transition temperature of typical amorphous PET is about 78°C, well above the Tg of any adhesive, which requires the Tg below room temperature. Additionally, a typical biaxially oriented PET film, after heat setting, has a high degree of crystallinity, usually over 55%, which further increases the PET matrix rigidity. As was typically done previously, many existing overlamination films admix low molecular weight UVAs in the adhesive layer, where the rigidity of the matrix is low. The UVAs dissolved into the low Tg adhesive layers do not surround the low molecular weight organic moieties with a rigid cage. This then allows for more rapid destruction of the UVAs themselves from free radical induced covalent bond scission. This degradation of the UVA in the adhesive system results in poor performance in stabilizing the graphic images. For the same reason, degradation of other, softer, low Tg films like plasticized PVC is faster when compared to stabilized PET film.

The other reason for the difference lies in the UVA itself. UV stabilized PET is a relatively new technology. It is desired to have a very high melting point of the UVA to protect the organic materials from volatilizing at the time of melt extrusion of PET. It is also desired that the UVA does not thermally degrade/oxide at high temperature so that no discoloration or harmful volatile gases are generated. This is very important since much of the PET film undergos multiple recycling as part of the commercial process of making plastic film. Because of its high processing temperature (up to 300°C) required to extrude PET, virtually all UV stabilizers will decompose to a quite extensive degree and produce fume/smoke during the film making process. The base PET film used to produce uvX™ utilize new, thermally stable UV stabilizers: high molecular weight, high melt temperature and highly heat resistant, yet maintaining high degree of absorptivity. These properties of the new UV stabilizers will protect the laminated images better since they are more difficult to evaporate, degrade or migrate out of the matrix compared to traditional UV stabilizers.

It is desirable to produce a UVA stabilized PET for overlamination graphics that is essentially color-free. Therefore, when overlaminated on a printed graphic, the color of the base film does not change the color of the graphic output. The low wavelength end of visible light (400-450nm) of the UV transmittance of uvX™ film is very flat (Figure 3), indicating that there is no absorption thus no color in the film itself. Many of the overlamination films absorb in the near 400-nm visible area, especially dyed PET, which causes the film visibly yellow. We tested the white background color change of some wide format media after laminating with a variety of commercially available overlamination films. uvX™ was again best in term of color change. Additionally, the white background color change of uvX™ was also the least after exposure in the weatherometer.

Conclusions

UV stabilized PET, i.e. polyester films, were prepared with dramatically improved weathering characteristics when compared to normal PET film bases. When constructed as an overlamination film base via PSA coating the material, exceptional image longevity enhancement has been determined. In fact, as of the date of publication of this paper, the author's could locate no material that improved image stability more than this technology, without yellowing. The many advantages, including the environmental friendliness of PET when compared to highly plasticized PVC films should make the UV stabilized PET overlamination film the choice of overlamination film in the near future.[6]

References

1. Niemoller, A., Becker, A. "Interactions of ink jet inks with ink jet coatings" in *IS&T's NIP 13*, p.430, 1997.
2. Owens, D.K., *J. of Applied Polymer Science*, Vol. **19**, p. 3315, 1975.
3. Marcotte, F.B., Campbell, J.A., Cleaveland, J.A, Turner, D.T. *Journal of Polymer Science*, Part A-1, Vol. **5**, p.481, 1967.
4. Fisher, R.M.; Ketola, W. "Exposure Test Results for Inkjet Inks in Interior Light Environments" in *Durability 2000*, ASTM-STP 1385.
5. Bucholz, B. "New Performance Standards Sets Durability Guidelines For Industry" in *The Big Picture Conference*, 2000, pages 72-73.
6. Pat Costner, PVC: A PRIMARY CONTRIBUTOR TO THE U.S. DIOXIN BURDEN (Washington, D.C.: Greenpeace, February, 1995).

Biography

Yijun Ye holds a Ph.D. degree in polymer chemistry from Rensselaer Polytechnic Institute in 1996, where he worked on electric filed effects on multiphase polymer systems. He has worked at Toray Plastics America in North Kingstown, RI since 1996. His work function has been on quality control-analytical chemistry and new product development of polyester films. He is a member of the American Chemical Society.

Steven J. Sargeant holds a Ph.D. in polymer synthetic chemistry from USC and was a post doctoral researcher at Cornell University in photoresist synthesis. He has received 16 US patents and written numerous publications in the fields of imaging chemistry, inkjet technology and polymer design. He is currently employed at Toray Plastics America as the manager of Research and Development.