Photofade In Polymer Films: Rate of Fade in Films and Solution

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Abstract

One of the most important attributes of color images is stability to exposure of light. Images that will be displayed indoors are usually subjected to accelerated testing by exposing them to simulated “daylight” that consists of radiation from a xenon lamp filtered through a soda-lime glass filter. Those images to be displayed outdoors are tested with a similar xenon lamp without the glass filter giving a higher exposure to ultraviolet light. The rate of photofade can depend on the type of polymer or dye, the availability of oxygen and humidity as well as the more obvious parameters of light intensity and temperature of the environment. We have attempted to investigate the rate of photofade of a yellow, magenta, and cyan dye in polycarbonate, polystyrene, polymethylmethacrylate, and a phenoxy resin to determine the impact of polymer type.

Our results include the photolysis of dyes in solution, as well as in coated films. The dyes exhibited no fluorescence in an ethanolic solution at 77° K. Phosphorescence observed in the polymers was attributed to impurities. Decay times indicate a very high probability of energy transfer from the polymer to cyan dye. Results on photofade show that polystyrene and phenoxy resin are significantly worse than polycarbonate and polymethylmethacrylate. Common addenda used to improve dye fade in polymers had very little positive effect. 2-aminophenol improves photofade for the cyan and magenta dye while zinc di-n-butyldithio-carbamate slightly improves cyan photofade.

Introduction:

When dye is transferred from a dye donor to the receiver in dye diffusion thermal transfer a dye concentration gradient exists in the receiver layer resulting in a high concentration at the surface. If no lamination of the image is done the very high surface concentration of dye remains where dye-dye interactions and exposure to oxygen in the air are very likely. Photomicrographs of cross-sections of receiver layer clearly indicate this as well as modeling studies done on dye diffusion thermal transfer systems.[1] Lamination of the printed image by application of heat causes dye at the surface of the receiver to diffuse further, thus reducing the high concentration of dye at the surface and reducing dye/dye interactions. The exposure of dye to oxygen is reduced due to the protective laminate. The environment of the dye has changed in two ways. It is at a lower concentration in the receiver layer and is exposed to the lower concentration of oxygen in the protective film. Interactions between the dye and polymer now become more important in the light stability of the dye.

Photofade mechanisms in laminated prints depend on interactions between the dye molecules as well as the dye molecules and polymer or impurities in the polymer. When the dyes are molecularly dispersed, previous work[2] has indicated that the mechanism of degradation depends greatly on the polymer environment. Photoreduction of dyes can be greatly aggravated by placing the dye in a material such as gelatin.

We have studied dye fade in solution with an aprotic solvent, acetonitrile, and a proton donating solvent, isopropanol to determine the propensity of dye radicals to abstract a proton during degradation. The results characterize the photodegradation of the dye alone.

Four polymers were chosen as representative of those that could be used in a thermal receiver layer – polymethylmethacrylate, polystyrene, polycarbonate and phenoxy resin. The dyes chosen represent three classes of dyes – azo, pyrazolone and naphthalene quinimine. Dye-polymer interactions were studied by forming films of the dye in polymer and following photodegradation by UV-Vis spectra.

Experimental:

Commercial polymer samples were chosen to be similar in molecular weight and were used without further purification. Polystyrene (#33165-1 MW Av. 45000), poly (Bisphenol A carbonate) (# 18162-5, MW 64000) and poly (Bisphenol A co-epichlorohydrin) (#18119-6 MW 40000) were obtained from Aldrich. Poly (methylmethacrylate) (# 037B, MW 75000) was obtained from Scientific Polymer Products.

Acetonitrile and isopropanol were both reagent grade while all tetrahyrofuran (THF) was HPLC grade without a stabilizer.

Eastman Kodak Company supplied the dyes used in this study. A yellow, magenta and cyan dye was used representing a pyrazolone, azo, and naphthalene quinimine type, respectively. The dyes were chosen as typical of those found in dye donors for thermal transfer.

The light source used at Manchester Metropolitan University (MMU) for generating photofade was a Microscal unit with a Thorn 500-watt lamp which simulates a warm daylight. The light source used for photofade at Eastman Kodak was a xenon lamp, 50 Klux illuminance, without a glass filter to simulate sunlight. The exposure cycle was continuous for the time indicated.

Photofade of dye solutions was done in quartz cuvettes that had been purged of oxygen by bubbling nitrogen through the solution prior to exposure. The cuvette was sealed and placed in the Microscal unit. The cuvette was removed at designated times to record the UV-Vis spectrum. Nominal concentrations of the dyes were approximately 10^{-5} M.

Thin films of dye in polycarbonate or phenoxy resin were prepared by coating the dye/polymer solution from THF onto a glass plate with a wire-wound rod. The dried film was lifted from the glass plate and suspended over a metal frame such that an UV-Vis spectrum could be recorded through the window of the frame. In the case of dye in poly (methylmethacrylate) or polystyrene the solution was coated onto microscope slides which were used as mounts for photolysis and analysis. The aim optical density for the dye in film was about 1.0. The dye to polymer ratio was approximately 45:1 and all addenda were added at 0.1% wt/wt based on polymer.

A Perkin-Elmer Lambda 12 spectrophotometer was used to obtain UV-Vis spectra. The photofade was calculated from absorbance at the peak wavelength of the dye. Fluorescence spectra were taken of the dyes in ethanol and as cast films using a powder sample attachment. The film was cast from tetrahydrofuran onto a glass, microscope slide cover which was mounted in the attachment. Phosphorescence spectra were determined using ethanolic solutions of the dyes as well as cast films that were tightly packed into the quartz sample tubes. All phosphorescence spectra ere done at 77 °K

Results and Discussion:

Dyes in Solution

The second derivative spectra of the dyes in solution showed very weak interaction between the dyes and acetonitrile or 2-propanol. Exposure of the dye solutions in the Microscal unit for five hours gave very little degradation of dyes in either solvent. The results indicate that in solution, free of oxygen, the dyes are quite stable and proton-donating solvents do not accelerate photofade.

Dyes in Polymer Films

Table 1 shows the crossover between dye films subjected to fade in the Microscal unit at MMU and the fade unit at Kodak Laboratories. Note the higher fade of the magenta dye in polystyrene and phenoxy resin and yellow dye in phenoxy resin with the Kodak light source. The higher fade is due to the increased UV content of the sunlight source.

Table 1. Percent Fade of Polymer Films in Microscal and Kodak Fade Units

Polymer	Dye	MMU Microscal	Kodak
POLYSTYRENE	CYAN	22	28
PHENOXY	CYAN	30	37
POLYCARBONATE	CYAN	7	3.8
PMMA	CYAN	6	5
POLYSTYRENE	MAGENTA	19	47
PHENOXY	MAGENTA	15	75
POLYCARBONATE	MAGENTA	5	11
PMMA	MAGENTA	6	11
POLYSTYRENE	YELLOW	15	7
PHENOXY	YELLOW	9	32
POLYCARBONATE	YELLOW	11	12
PMMA	YELLOW	6	5

Table 2 Rate Constants for Photofade of Dye in Polymer Films

$k \times 10^4$ (SEC^{-1})

	DYES		
POLYMERS	CYAN	MAGENTA	YELLOW
PHENOXY	33	6.3	5.7
POLYCARBONATE	2.4	0.7	4.3
POLYSTYRENE	20	11	8.2
PMMA	9.8	2.8	8.4

Table 2 gives the calculated first order rate constants for the photofade of dye the polymer films. It is obvious that the cyan dye fades much faster than either the magenta or yellow dyes in the same polymer film. The result would be a color balance shift to the red of a neutral gray image. Selection of the polymer, such as polycarbonate, reduces the rate of fade but not the shift in color balance. The question becomes whether the addition of an addendum, or stabilizer, could improve the fade of one dye in a polymer without affecting the other two dyes.

The addenda added to the polymer film were sodium phenylphosphinate, zinc dibutyldithiocarbamate, 2-aminophenol, zinc dinonyldithiocarbamate and the zinc salt of shell acid. The results for the photofade of cyan dye in the Microscal unit for 200 hours are shown in Table 3. A difference of 6 percent fade units can be considered as real. Comparison of the photofade for polymer films with addenda to the control indicate that there is little or no improvement seen. Table 4 shows the results of the same experiment but using the magenta dye. When the photofade for the control is high such as in the case of phenoxy resin or polystyrene the addenda seem to improve the light fade of the system. The results for photofade of the yellow dye are shown in Table 5. Here the photofade exhibits no improvement or worse fade than the control when addenda are added. If the objective is to improve the photofade and to make fade more neutral, then no one addendum used in this work will accomplish that purpose. The fade of cyan and magenta may be improved but yellow becomes worse.

Table 3 Percent Fade of Cyan Dye Film with Addenda

ADDENDA	PHENOXY RESIN	POLY-CARBONATE	POLY-STYRENE	PMMA
Control	51	5	36	16
Na Phenyl Phosphinate	56	4	31	15
ZnDBDT Carbamate	57	5	31	13
2-amino phenol	47	4	33	16
ZnDiNDT Carbamate	46	4	31	13
Zn Salt Shell Acid	55	6	30	16

Table 4 Percent Fade of Magenta Dye Film with Addenda

ADDENDA	PHENOXY RESIN	POLY-CARBONATE	POLY-STYRENE	PMMA
Control	10	2	21	5
Na Phenyl Phosphinate	6	2	13	6
ZnDBDT Carbamate	4	3	18	6
2-amino phenol	4	3	14	5
ZnDiNDT Carbamate	5	3	17	6
Zn Salt Shell Acid	6	2	22	5

Table 5 Percent Fade of Yellow Dye Film with Addenda

ADDENDA	PHENOXY RESIN	POLY-CARBONATE	POLY-STYRENE	PMMA
Control	10	9	17	16
Na Phenyl Phosphinate	6	9	16	13
ZnDBDT Carbamate	18	11	18	21
2-amino phenol	6	8	14	12
ZnDiNDT Carbamate	22	10	21	20
Zn Salt Shell Acid	9	10	18	12

Fluorescence and Phosphorescence Spectra:

Impurities in the polymers may well influence the mechanism and rate by which dyes photodegrade. We attempted to measure the fluorescence of the polymers with and without dye present to determine the possibility of energy transfer between polymer and dye. The dyes exhibited no fluorescence in either solution or as powders. All of the polymers exhibited fluorescence. One complicating factor is the absorption of the polymer emission by the dye when both are in the same film. Given the emission spectrum of the polymer alone and the extinction coefficient of the dye at the same wavelength, the degree of absorption by the dye can be estimated. All of the dye-polymer combinations were evaluated, but only the decrease in emission of the polystyrene in the presence of magenta dye could be attributed to energy transfer between the two. There is a significant decrease in the intensity of emission from polystyrene upon addition of magenta dye.

Table 6 gives the peak wavelength of phosphorescence of the polymers as thin films containing cyan dye. The dyes in absence of polymer gave no phosphorescent emission. The phosphorescence comes from the polymers, or more likely impurities present in the polymer. The rate of decay of phosphorescence is not influenced by competitive absorption of emitted light by the dye. Consequently, it is much easier to measure transfer of energy from the polymer or its impurities to the dye by the decrease in the rate of decay. Unfortunately, the emission with cyan dye in PMMA or polystyrene is decreased to such an extent that noise makes the calculation of a decay rate difficult. The decrease in decay rate with polycarbonate and phenoxy resin indicates an efficient transfer of energy from these polymers to the cyan dye.

Table 6 Phosphorescence Decay Times of Polymer Emission

Polymer/dye	Peak Wavelength (nm)	Intensity	Decay Time (msec)
PMMA	450	18	9.9
PMMA/cyan	--------	<0.3	--------
Polystyrene	425	24	7.1
Polystyrene/cyan	450	3.8(spike)	--------
Polycarbonate	430	40	15.5
Polycarbonate/cyan	430	<0.3	1.9
Phenoxy resin	440	80	32.7
Phenoxy/cyan	440	3.5	7.2

Note: Dyes did not show any phosphorescence in ethanol at 77° K.

Conclusions

Very weak interactions exist between the dyes and either acetonitrile or 2-propanol indicating little impact of labile hydrogen atoms in the polymer on light fade. Photodegradation of the cyan dye is weakly dependent on the intensity of ultra-violet light in the four polymers tested while the opposite is true of the magenta dye. The magenta dye is very susceptible to fade in phenoxy resin and is similar to the yellow dye in this aspect.

2-aminophenol improves fade of the magenta dye in phenoxy resin and polystyrene while the same material improves yellow dye fade in phenoxy resin and polycarbonate.

Zinc dinonyldithiocarbamate improves the fade of cyan dye in all four of the polymers tested. It becomes obvious that stabilization of all three dyes in one polymer system would require the addition of more than one additive. It is also important that any one of the additives not aggravate the fade of one dye while improving that of another. In general the selection of a polymer such as polycarbonate gives the best overall stability without the presence of addenda.

We have found that the intensity of fluorescence is not a good measure of energy transfer because of the readsorption of the emitted light by the dye. Phosphorescence decay times are not dependent on readsorption of emitted light by the dye and are the preferred method to measure energy transfer between polymer and dye. Only when the intensity of emission due to phosphorescence falls to such a low value that decay times are difficult to calculate is there a problem. In our work phosphorescence decay times indicate a high probability of energy transfer from each polymer used or its impurities to the cyan dye.

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Biography

William H. Simpson (Bill) received his Bachelor of Science in Chemistry from the College of William & Mary in Virginia and his Ph.D. in Physical Chemistry from the University of Pennsylvania. He has worked on the development of instant film at Polaroid and micro-encapsulated imaging systems at Mead Imaging. Since arriving at Kodak Bill has worked on the development of dye diffusion thermal transfer and laser imaging systems. He has focused on the keeping properties of prints and the development of donor and receiver materials. He has a total of 24 patents in imaging technology and is a member of the Kodak Distinguished Inventors Gallery. Bill has been a member of IS&T for 29 years.