Studies towards Lightfast Automotive Dyes for Polyester

Harold S. Freeman, Natacha Berthelon, and Laura C. Edwards
Fiber and Polymer Science Program
North Carolina State University, Box 8301
Raleigh, NC 27695, USA
Harold_Freeman@ncsu.edu

ABSTRACT

This paper provides an overview of studies conducted in our dye chemistry laboratories that were directed towards the design, synthesis, and evaluation of dyes for polyester fibers for applications requiring high lightfastness. Presented are results from the early studies in our program that involved characterizing the chemistry associated with the light-induced (photo) degradation of azo, anthraquinone, and nitrodiphenylamine disperse dyes in an ester environment. This is followed by a summary of molecular design efforts based on results from dye photodegradation experiments. In this case, results pertaining to the utility of built-in photostabilizer groups for enhancing disperse dye lightfastness (resistance to light-induced fading) are discussed. Special attention is given in this paper to studies in which the effects of natural and artificial light on oriented polyester films following the application of azo, anthraquinone and nitrodiphenylamine dyes were assessed. This work was part of an investigation aimed at determining the contribution of polyester to the fading of disperse dyes. In this regard, dyed polyester films were exposed to sunlight from two regions in the United States and to the artificial light of an Atlas Weatherometer. The results of the different exposures indicate that artificial light exposures were far more damaging to the polymer host than natural light. It was also apparent that a significant level of dye fading could be attributed to substrate degradation.

Keywords: dye, fading, lightfastness, polyester films, exposure

1. Background

It is both ironic and unfortunate that the very types of processes responsible for the colors we see on textiles are also responsible for their demise when the adsorbed dyes are exposed to sunlight for prolonged periods. Color is seen whenever an object absorbs light of a given wavelength in the visible region (400-700 nm) of the electromagnetic spectrum and reflects the remaining incident light to our eyes. The colors we perceive as a consequence of these processes are summarized in Figure 1[1]. Note that the colors seen are complementary to the one absorbed. Invariably, organic compounds, including the colorants used to dye textile fibers, also absorb light in the ultraviolet (UV) region (200-400 nm). See, for example, the Pisystem[2] calculated absorption spectrum for Disperse Blue 14 in Figure 2, where the absorption at 600 nm is responsible for color and those at 324 nm and 385 nm probably contribute most to fading since window glass filter systems typically give a 310 nm cut off.

Wavelength Absorbed (nm	Color Absorbed	Color Seen
400 - 435	Violet	Yellow-Green
435 - 480	Blue	Yellow
480 - 490	Green-Blue	Orange
490 - 500	Blue-Green	Red
500 - 560	Green	Purple
560 - 580	Yellow-Green	Violet
580 - 595	Yellow	Blue
595 - 605	Orange	Green-Blue
605 - 700	Red	Blue-Green

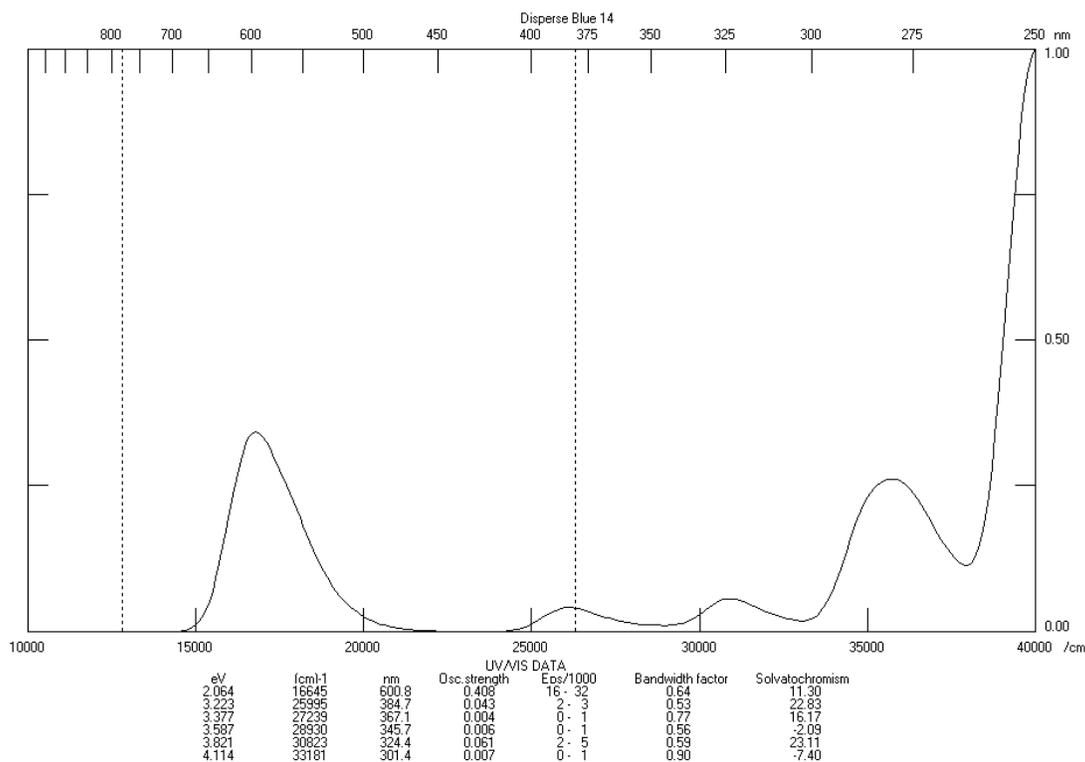Figure 1. Colors perceived following visible light absorption.

eV	(cm)-1	nm	Osc.strength	Eps/1000	Bandwidth factor	Solvatochromism
2.064	16645	600.8	0.409	16 - 32	0.64	11.30
3.223	25995	384.7	0.043	2 - 3	0.53	22.83
3.377	27239	367.1	0.004	0 - 1	0.77	16.17
3.587	28930	345.7	0.006	0 - 1	0.56	-2.09
3.821	30823	324.4	0.061	2 - 5	0.59	23.11
4.114	33181	301.4	0.007	0 - 1	0.90	-7.40

Figure 2. Calculated absorption spectrum for Disperse Blue 14.

Just as the absorption of UV light by our skin is harmful to the cells comprising human tissue, the absorption of this type light by organic dyes can modify the molecular structure of dyes to cause color changes/fading. Interestingly, the same types of compounds used to protect our skin against UV damage can be used to control the dye fading process.

It has long been known that the fading of dyes on a polymer substrate is influenced by:

- the structure of the dye
- the structure of the substrate
- the presence of moisture and atmospheric contaminants
- temperature
- the properties of the light source
- the physical state of the adsorbed dye

It is also clear that studies in this area have focused primarily on the relationships between dye structure and lightfastness and the molecular transformations that take place when dyes undergo fading. The majority of these studies were conducted by using solvents as models for textile substrates, and in this regard, ethyl acetate, dimethyl formamide, and methanol have been used as models for polyester, polyamide, and cellulosic substrates, respectively. The details of such studies have been reviewed[3], and a somewhat older reference summarizes studies involving polymeric media[4]. In a more recent review paper, the photochemistry of disperse dyes has been summarized[5]. This is important in the present context, as disperse dyes are the only dyes suitable for dyeing polyester fibers.

With regard to the influence of disperse dye structure on lightfastness, results of studies have shown that anthraquinone dyes are generally more lightfast than their azo counterparts. This is especially true for red and blue anthraquinone dyes that have an –OH (hydroxyl) group in one or more of the α-positions of the anthraquinone ring system, examples of which are Disperse Red 60 and Blue 27 (Figure 3). The lightfastness of these dyes arises from their ability to undergo intra-molecular proton transfer from the –OH group to the adjacent C=O (carbonyl) group following light absorption in the UV region. This is an *internal conversion* process, as the absorbed UV light energy is dissipated as harmless heat.
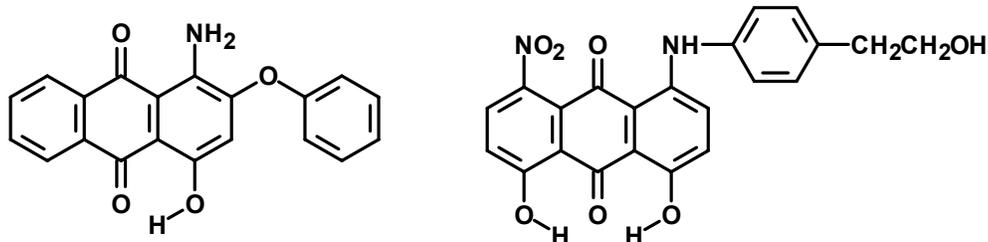

Figure 3.   Structures of two lightfast anthraquinone disperse dyes for polyester: Disperse Red 60 (left) and Disperse Blue 27 (right).

The small number of lightfast azo disperse dyes include Disperse Red 167:1 (Figure 4), which takes advantage of intramolecular hydrogen bonding (H-bonding) between the azo (-N=N-) bond and adjacent –NH group to stabilize the dye against UV light degradation. Similarly, lightfast yellow dyes for automotive fabric have proton transfer as an internal mechanism for UV stabilization. An example is Disperse Yellow 86 (Figure 4).
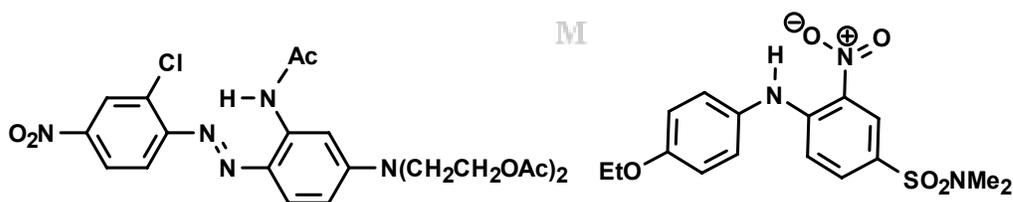

Figure 4.   Structures of two lightfast disperse dyes for polyester: Disperse Red 167:1 (left) and Disperse Yellow 86 (right).

UV absorbers are co-applied with disperse dyes to give lightfastness at levels essential to long-lived automotive body

fabric. These compounds enhance dye lightfastness by an *energy transfer* mechanism[4]. In this regard, the energy taken on by dye molecules following UV light absorption is transferred to UV absorber molecules, and the transferred energy is subsequently dissipated via internal conversion. While a number of commercial photostabilizers can be used to protect disperse dyes on polyester fibers, commonly used agents are hydroxybenzotriazoles and hydroxy-benzophenones (Figure 5), where R_1 is a linear alkyl group and R_2 is usually methyl or *t*-butyl.
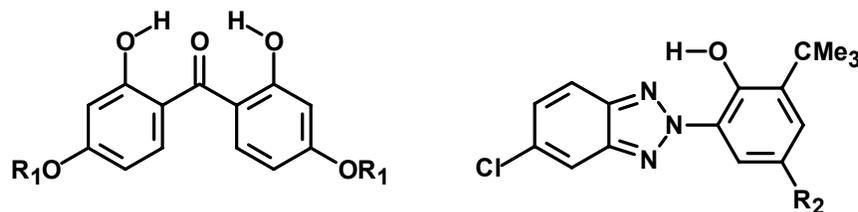
Figure 5.   Structures of benzophenone (left) and benzotriazole (right) type UV stabilizers for disperse dyes on polyester.

On the other hand, it is also known that certain structural features lead to poor lightfastness in disperse dyes. In this case, the presence of 1) *N*-hydroxethyl groups in azo or anthraquinone dyes[6], 2) *ortho*-nitro groups in azo dyes[3,7], and 3) groups leading to azoxy formation[3,8] cause reduced lightfastness. Examples of dyes that fit into this category are shown in Figure 6.
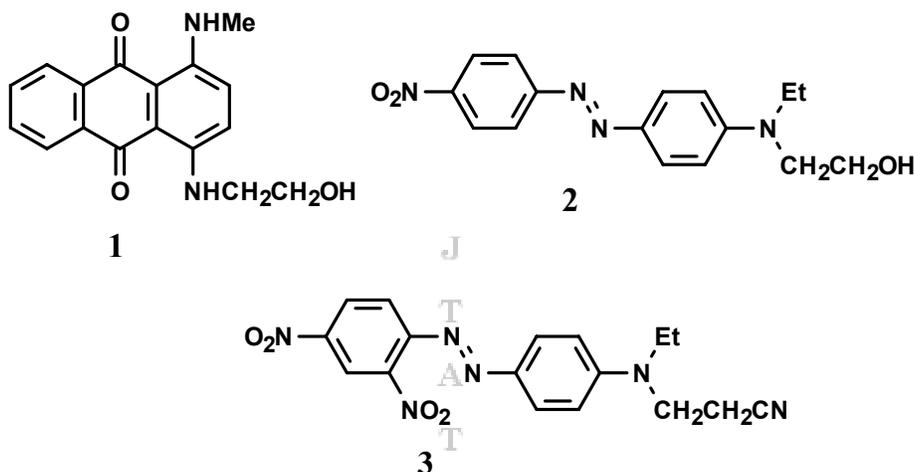

Figure 6.   Examples of disperse dye structures having low lightfastness on polyester.

The above types of background information were used as a springboard for our studies in this area that began in the mid-1980s. A summary of this work is presented in section 2.

2.   Dye Considerations

The initial studies in our program focused on two areas: 1) determination of the reactions associated with the photodegradation of automotive disperse dyes on polyester fabric and 2) design and synthesis of lightfast disperse dye analogs of commercial prototypes. In both cases, dyes such as **4-7** were used as prototypes, and

light exposures were conducted according to a published method for automotive dyes[9]. With regard to dye degradation, it was determined that Red 91 produced products arising from cleavage of the alkyl group, oxidation of the substituted ring to an iminoketone system, and substitution of the amino group by a hydroxyl group. Red 167:1 underwent reductive cleavage of the azo bond to give the corresponding aromatic amines. Like Red 91, Blue 56 produced products arising from substitution of the amino groups by a hydroxyl group. Dye **7a** (Yellow 42) underwent cleavage of the sulfonamide bond, producing aniline, which in turn was oxidized to give the fabric a darker hue[10].
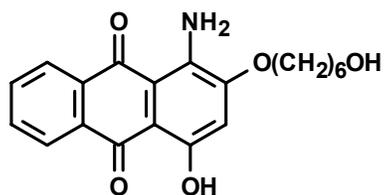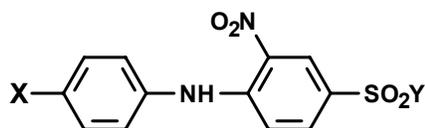

4 (C.I. Disperse Red 91)
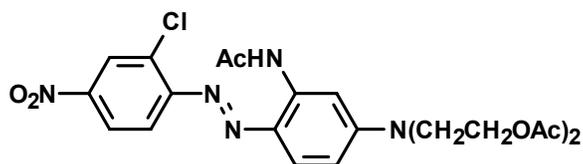
5 (C.I. Disperse Red 167:1)
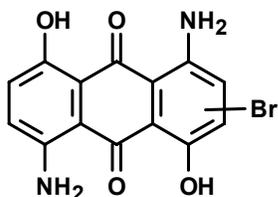
6 (C.I. Disperse Blue 56)

7 (X/Y = **a**: H/NHPh; **b**: OEt/NMe$_2$)

In view of the aforementioned results and the commercial practice of using UV absorbers to enhance the lightstability of disperse dyes on polyester, we elected to develop some disperse dye analogs containing built-in photostabilizers[11-14]. This led to the synthesis of experimental disperse dyes such as **8-14**, in which benzophenone, benzotriazole, hindered amine and oxalanilide groups were employed to improve the stability of the parent dye. We found that the lightfastness of Red 167:1 (**5**) on polyester was best improved by incorporating an oxalanilide stabilizer (cf. dye **8**), with X = ethyl (Et) giving the best results[14]. In this case, the azo (–N=N–) group was stabilized by intramolecular H-bonding with the adjacent N–H group (Figure 7). This critical feature was lost when experimental dye **9a** was produced, as x-ray crystallography showed that the hydroxybenzoyl group does not lie in the same plane as the azo group[12] (cf. Figure 7). This pre-empted H-bonding between the azo group and the anticipated UV (hv) light-induced enol form (**9b**) of the *ortho*-hydroxybenzophenone moiety. While intramolecular H-bonding was restored when dye **10** was produced, this dye had to be applied by thermosol dyeing, as it decomposed in the dyebath during exhaust dyeing at 130° C (i.e. under pressure). Forming the methyl ether of the phenolic (–OH) group (cf. dye **11**) solved the thermal stability problem but did not enhance lightfastness.
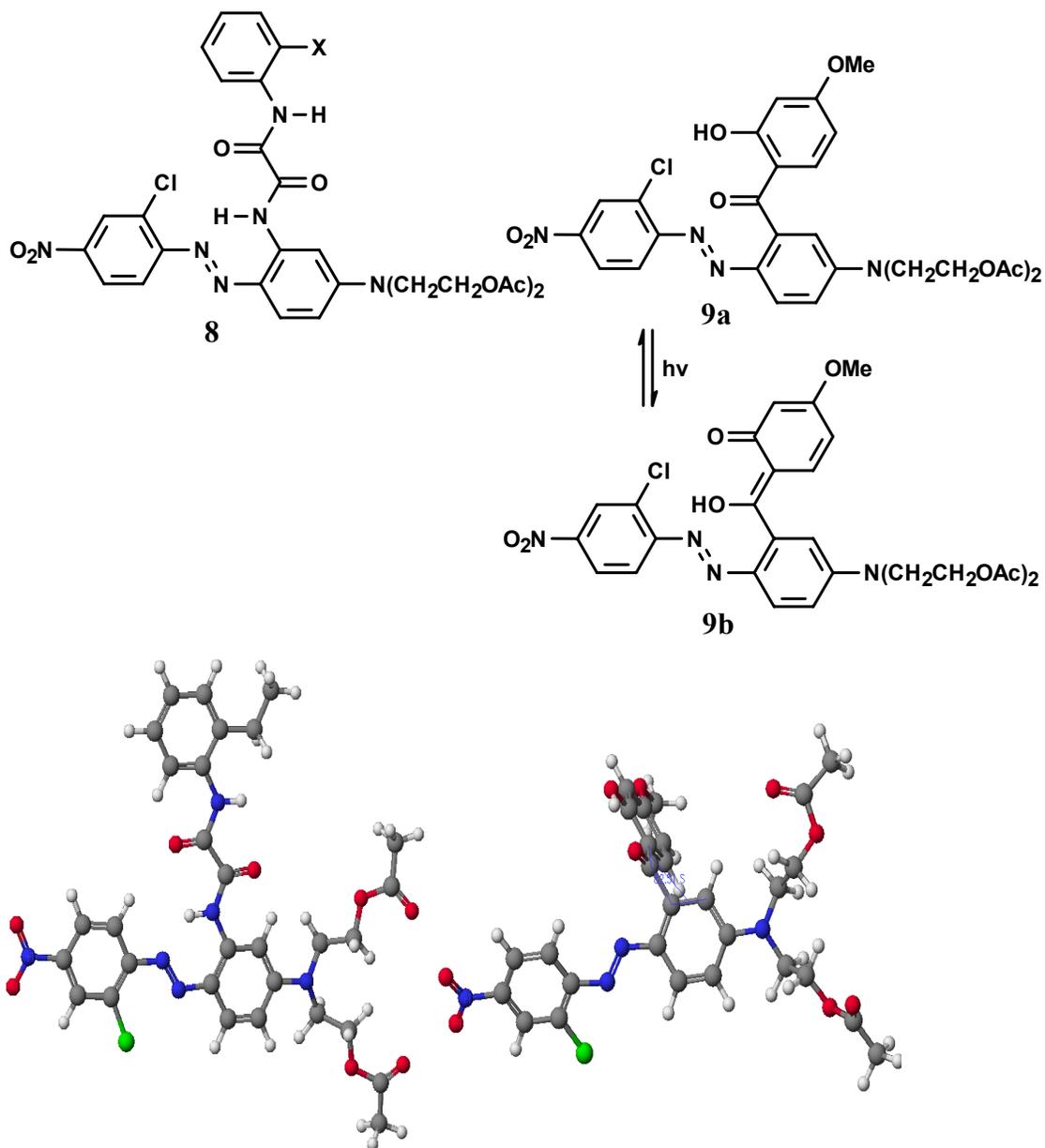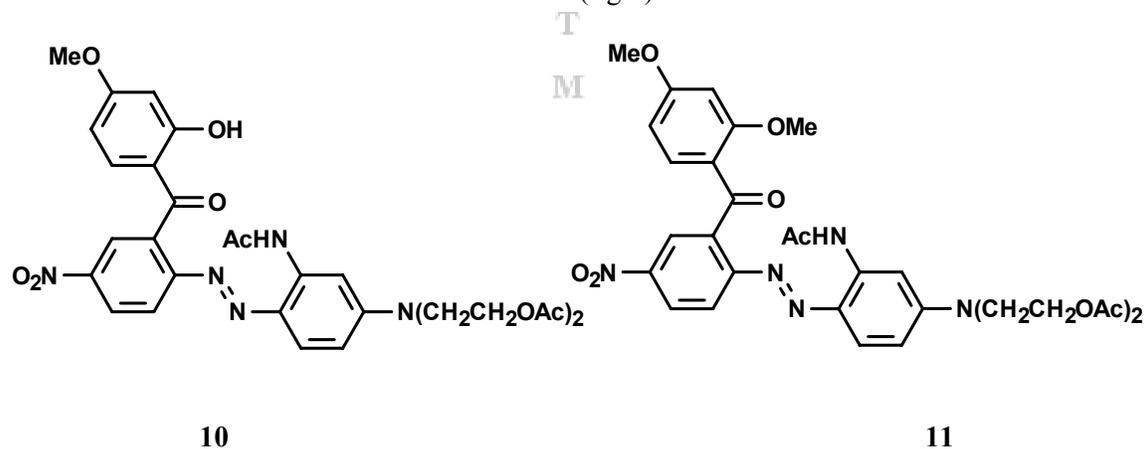
Figure 7. Geometry optimized structures showing the molecular conformations for dyes **8** (left) and **9a** (right).

The lightfastness of nitrodiphenylamine dye **7a** (Yellow 42) was improved by forming dye **12**, which contains a built-in benzophenone stabilizer moiety. On the other hand, incorporating a benzotriazole moiety (e.g. **13**) or hindered amine moiety (e.g. **14**) did not have a beneficial effect. It was anticipated that the latter structural variation would prevent the oxidation of aniline that accompanied the fading of Yellow 42. With regard to the inferiority of dye **13**, it is possible that the absence of a bulky group (e.g. t-butyl) *ortho* to the OH group reduced the efficiency of intramolecular proton transfer in the excited state. The synthesis of a structure containing such a group proved impractical.

12

13

14
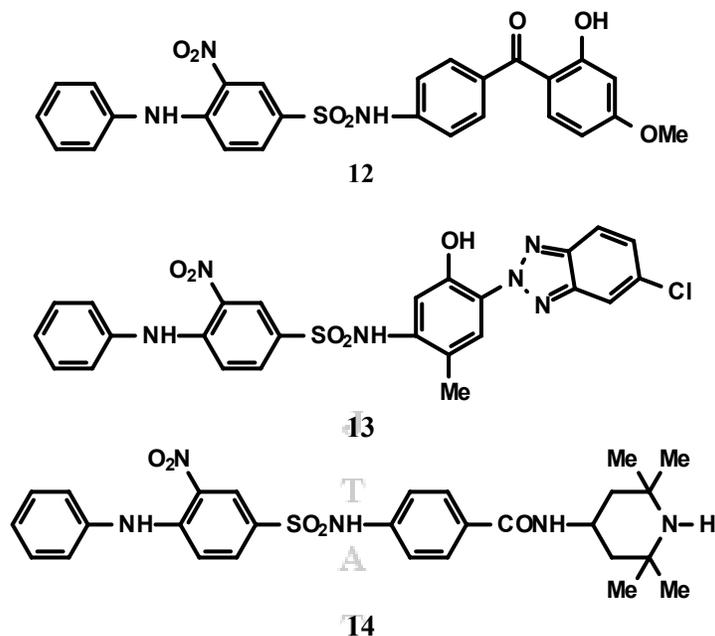
It is clear from our studies in this area, that the design of lightfast disperse dyes containing a built-in UV absorber group is a viable approach to enhancing the lightfastness of existing commercial azo disperse red and nitrophenylamine yellow dyes. It should be noted that the choice and location of the stabilizer group are critical to success. While it was also possible to synthesize anthraquinone disperse blue dyes with a built-in stabilizer group (cf. Figure 8) the existing high dye lightfastness was not further enhanced.
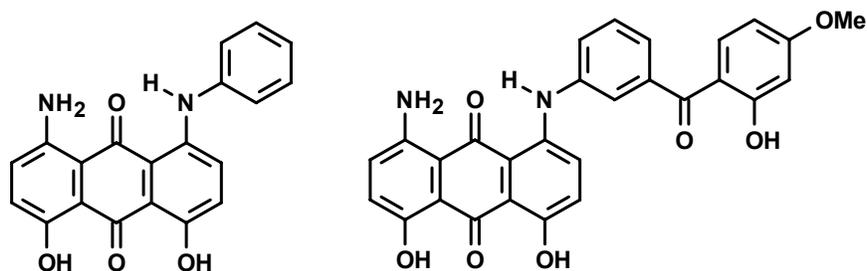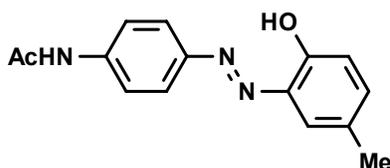

Figure 8.   Structure of the automotive dye Disperse Blue 77 (left) and its experimental analog (right).
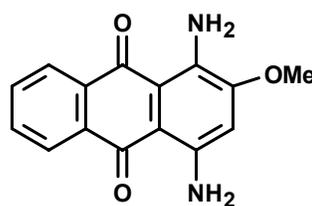
3. Substrate Considerations

Although much is known about the ability of certain dyes to cause phototendering of fabrics to which they are applied[4], very few studies have been devoted to assessing the contribution(s) of the polymer-based substrate to the photodegradation of adsorbed dyes. Our dye chemistry group became interested in this subject following studies involving the irradiation of several commercial disperse dyes on polyester films using natural (South Florida and Arizona sunlight) and artificial light (xenon arc weatherometer)[15]. Outdoor studies were conducted at 98° C (Arizona) and 99° C (South Florida) without humidity control, and the dark/light cycle was environmentally dependent. For xenon arc exposures a chamber temperature of 89° C was used, along with 50% relative humidity, and controlled light/dark cycles (3.8h light/1h dark). The disperse dyes employed included those suitable (e.g. Red 91, Red 167:1, Blue 56 and Yellow 42) and unsuitable (e.g. Red 1, Blue 3, Yellow 3 (**15**) and Red 11 (**16**) for meeting the lightfastness requirements of automotive interior fabric. Representative photographs of the center of films obtained following 451kJ light exposures and Scanning Electron Microscopy (SEM) studies are shown in Figures 9-11. Just prior to SEM analysis, the films were folded into quarters, placed under a weight for 3 min, and reopened.

15 (C.I. Disperse Yellow 3)

16 (C.I. Disperse Red 11)

While color loss was evident after all exposures, extensive polymer degradation appeared, as deep cracks, only after xenon arc exposures. When non-automotive dyes were used, color loss was often accompanied by objectionable hue changes, as illustrated in Figures 9 and 10. The hue shifts indicate that natural and artificial light caused structural changes in the dye molecules. In prior studies[6], we found that cleavage of the N-CH$_2$CH$_2$OH group and oxidation of the N-methyl group of Blue 3 took place during xenon and carbon arc exposures. Such changes would produce a red color in this case. For automotive grade dyes, on-tone color changes were usually observed rather than hue shifts. In the case of Yellow 42 (Figure 11) and Blue 56 a darkening of the shade was observed. As indicated above, we believe this change is due to the formation and oxidation of aniline during light exposures.
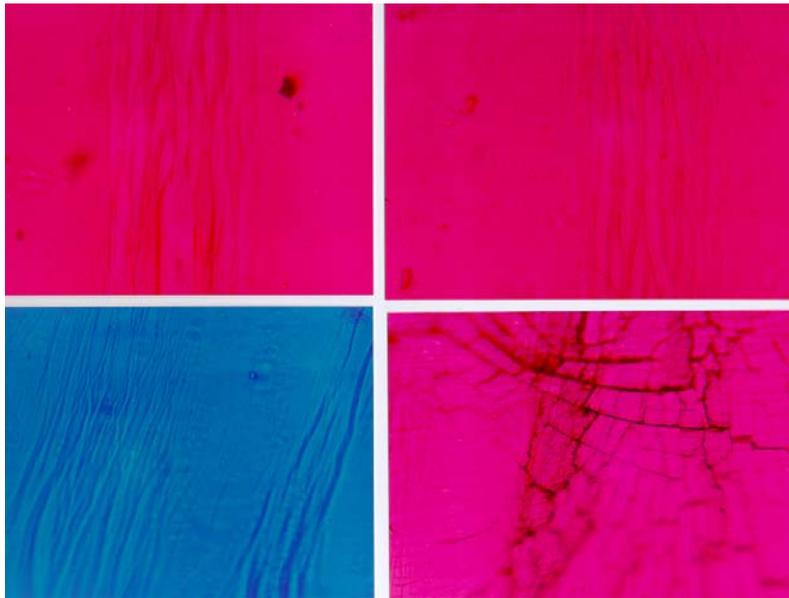
Figure 9.   Photomicrographs of Disperse Blue 3-dyed oriented polyester films. Clockwise from bottom left: unexposed film, 451 kJ Florida exposure, 451 kJ Arizona exposure, and 451 kJ xenon arc exposure.
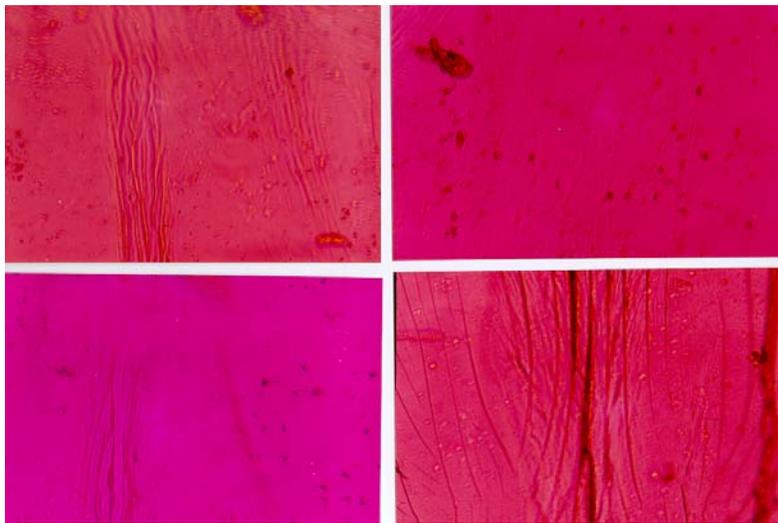

Figure 10.   Photomicrographs of Disperse Red 11-dyed oriented polyester films. Clockwise from bottom left: unexposed film, 451 kJ Florida exposure, 451 kJ Arizona exposure, and 451 kJ xenon arc exposure.
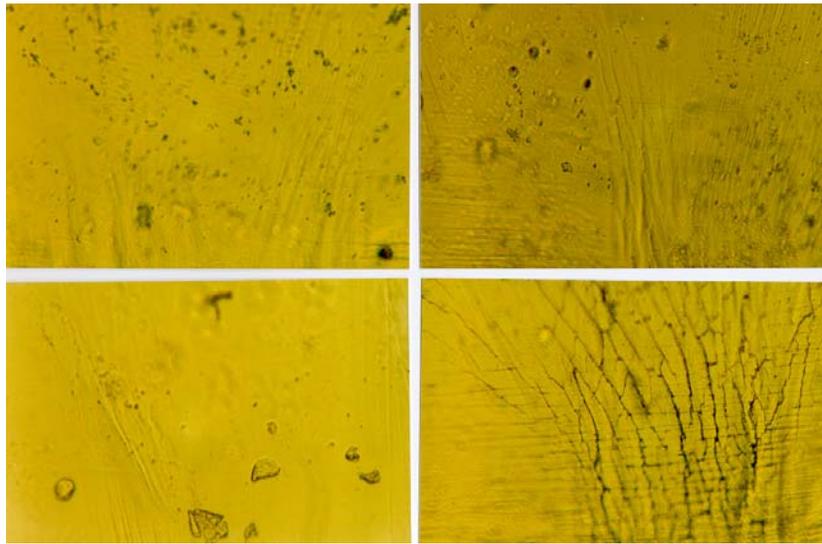
Figure 11. Photomicrographs of Disperse Yellow 42-dyed oriented polyester films. Clockwise from bottom left: unexposed film, 451 kJ Florida exposure, 451 kJ Arizona exposure, and 451 kJ xenon arc exposure.

Though not shown in this set of photographs, when undyed polyester films were irradiated, slight yellowing accompanied polymer degradation. However, it is clear from the present photographs that considerably more polymer degradation occurred during artificial light exposures than during natural light exposures. This was true despite the photostability of the dyes applied.

The observation of film integrity changes during the irradiation of 100 μm type D Mylar (polyester) film, led to our investigating the possible effects of polyester degradation on disperse dye fading[16,17]. In this regard, the possible relationship between polymer photodegradation and dye fading was investigated using the sequence of steps outlined in Figure 12. The experimental design involved the preparation of two sets of films. The first set was dyed at a 1% shade depth before light exposures. The second set was exposed undyed for one-half of the standard irradiance level, i.e. 112.8 kJ/m^2 (xenon arc) or 15,000 Langleys (Arizona), and then dyed (1% w/w) and exposed for an additional 112.8 kJ/m^2 or 15,000 Langleys (Lgs).

```
                        ┌─────────────┐
                        │  PET Film   │
                        └─────────────┘
```
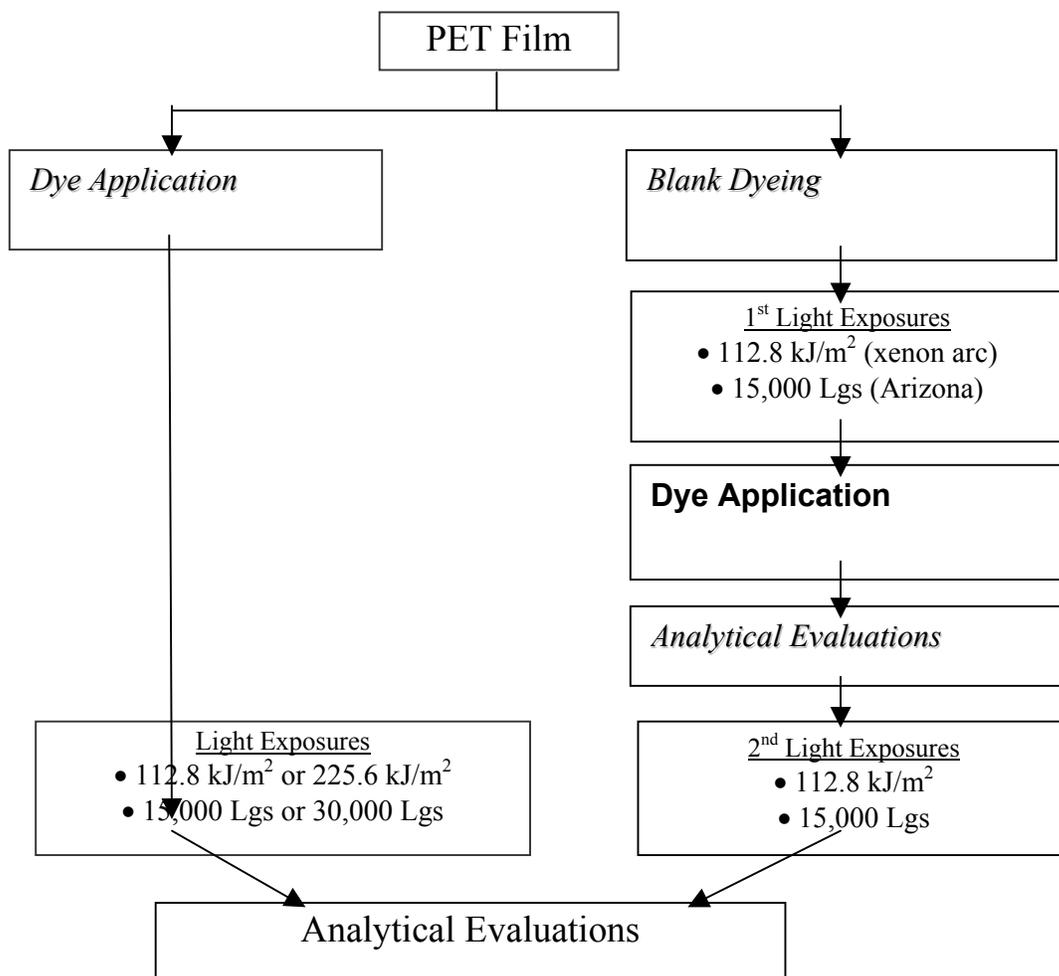
Fig 12. Experimental design used in the substrate-considerations aspect of this study.

Absorption Spectra

Figures 13-14 show summaries of absorption data from the evaluation of undyed polyester film and polyester films dyed with six representative disperse dyes (**1**, **2**, **5-6**, **7b** and **15**). The absorbance values were recorded at the absorption maximum of each dye. It can be seen from Figure 13 that the intensity of the absorption maximum, in decreasing order, was generally: 1) Unexposed, dyed polyester film, 2) polyester film exposed to 112.8 kJ/m^2 after dyeing (Post-Exp. 1), 3) polyester film exposed to 225.6 kJ/m^2 after dyeing (Post-Exp. 2), and 4) polyester film

exposed to 112.8 kJ/m^2 before dyeing and then for another 112.8 kJ/m^2 after dyeing (Pre-Exp.). The lone exception to the 1>2>3 pattern was Yellow 3 (Y3). In this case, pre-exposure of polyester had no adverse effect on dye degradation and the 225.6 kJ exposure caused the highest level of fading. While the fading of Red 1 (R1) followed the 1>2>3 pattern, the 225.6 kJ exposure was the most damaging. Nevertheless, these results do suggest that polyester photodegradation has an adverse effect on disperse dye stability. The latter point is further illustrated in the graph in Figure 14. In this case, absorption spectra were recorded on

dyeings obtained following pretreatment of polyester with the UV absorber Tinuvin 326 (**17**) prior to light exposures. It can be seen that the adverse effects of polyester degradation were prevented when dyes Red 91, Blue 56, Yellow 86 and Yellow 3 were applied. The two dyes that have inherently low lightfastness (Blue 3 and Red 1) were still adversely affected by polyester degradation, though to a lesser degree than when no UV absorber was used.
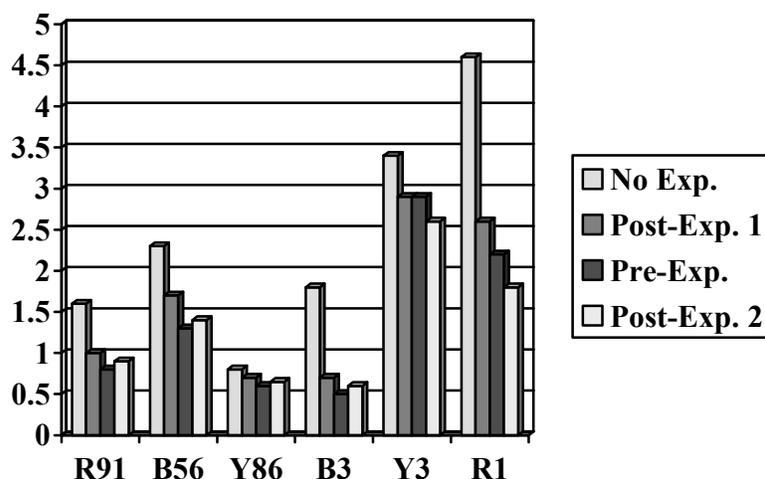

Figure 13. Absorbance values for 1% shades of dyes **1**, **2**, **5-6**, **7b** and **15** on polyester a) before exposure, b) following a 112.6 kJ exposure, c) following a 112.6 kJ exposure of pre-exposed polyester, and d) following a 225.6 kJ exposure.
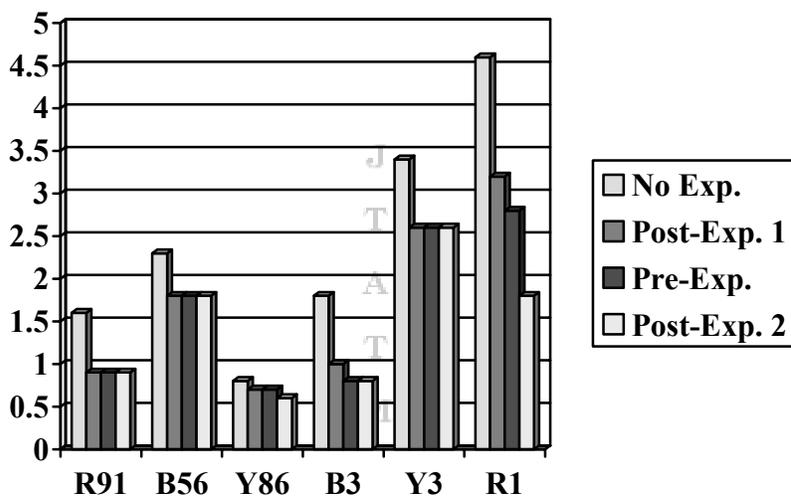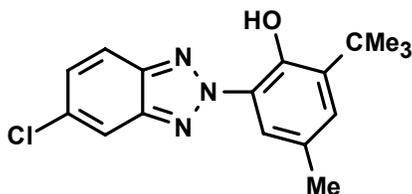

Figure 14. Absorbance values for 1% shades of dyes **1**, **2**, **5-6**, **7b** and **15** on UV absorber-treated polyester a) before exposure, b) following a 112.6 kJ exposure, c) following a 112.6 kJ exposure of pre-exposed polyester, and d) following a 225.6 kJ exposure.
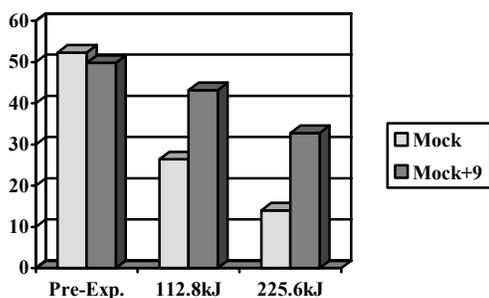
17 (Tinuvin 326)

Experiments were also conducted that involved the application of Tinuvin 326 to undyed polyester films <u>after</u> an initial 112.6 kJ light exposure but <u>before</u> exposing the dyed, pre-exposed films. In this case, the results indicated that dye fading was reduced to a greater degree when Tinuvin 326 was introduced prior to irradiating the undyed film than when it was employed during dye application on pre-exposed polyester films.

In studies involving natural versus artificial light, Arizona sunlight generally caused less fading of dyed films than xenon arc light (except for Blue 3 and Red 1). This is probably due to the greater humidity and higher irradiance level in the case of the artificial light exposures. For the two exceptions, dye fading was severe under all conditions.

Tensile Strength

The addition of Tinuvin 326 before the initial light exposure had a beneficial effect on the strength of polyester films that were exposed prior to dyeing. On the other hand, the use of Tinuvin 326 when dyeing pre-exposed films did not prevent further polymer degradation, as comparable breaking strengths were obtained whether or not Tinuvin 326 was used in dyeings performed after an initial light exposure in the absence of Tinuvin 326. Interestingly, films exposed to Arizona sunlight showed little or no loss in elongation at break, even after the harshest exposure (30,000 Lgs). This is illustrated in Figure 15.

When comparing dyed versus undyed films, it was found that the irradiated dyed films showed less strength loss than their undyed counterparts. This was true for artificial and natural light. It is not yet clear how the dyes employed provided this protective effect.
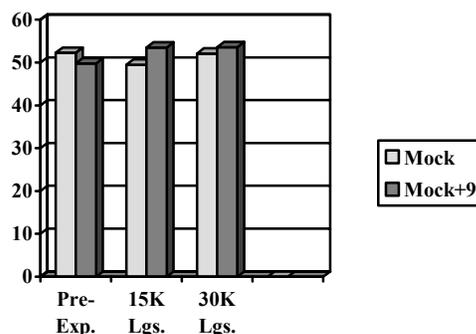
Figure 15. Elongation (nm) at break for mock-dyed films following xenon arc (left) and Arizona (right) exposures.

The following is clear from this aspect of our studies:

- The photodegradation of polyester contributes to the fading of adsorbed disperse dyes, as polyester films irradiated before dyeing showed more color loss than films that were dyed and then irradiated.

- The use of a benzotriazole UV absorber reduces polyester degradation, resulting in less dye degradation.
- The presence of automotive disperse dyes can have a protective effect on the photodegradation of polyester, as less strength loss was observed following the irradiation of dyed versus undyed films.

- Accelerated fading using xenon arc light has a far more destructive effect on

polyester than sunlight.

References

1. E. N. Abrahart, <u>Dyes and their Intermediates</u>, Chemical Publishing, New York, 1977.
2. M.G. Hutchings, Dyes and Pigments, **29**(2), 95 (1995).
3. N. Kuramoto, in <u>Physico-chemical Principles of Color Chemistry</u>, A.T. Peters and H.S. Freeman, eds., Chapter 6, p. 196, Chapman & Hall, Scotland, UK, 254-292, 1996.
4. N. S. Allen and J. F. McKellar, <u>Photochemistry of Dyed and Pigmented Polymers</u>, Applied Science Publishers, London, 1980.
5. J. Lye and H.S. Freeman, Adv. Colour Sci. Technol., **2**, (1999).
6. H.S. Freeman and W.N. Hsu, Textile Res. J., **57**(4), 223(1987).
7. H.S. Freeman and S.A. McIntosh, Textile Res. J., **59**(6), 343(1989).
8. T. Kitao, Y. Watada, M. Matsuoka, and K. Konishi, Nippon Kagaku Kaishi, (4) 757 (1974).
9. J. E. Bullock and D. L. Garrett, J. Ind. Fabrics, **4**(2), 23 (1985).
10. B. L. Richardson, "Characterization of the Photodegradation Products of State-of-the-Art Disperse Dyes on PET Fabric", Unpublished Masters thesis, North Carolina State University at Raleigh, 1992.
11. H.S. Freeman, S-D. Kim, R.D. Gilbert, and R. McGregor, Dyes and Pigments, **17**(2), 83(1991).
12. H.S. Freeman and J.C. Posey, Jr., Dyes and Pigments, **20**(3), 147(1992).
13. H.S. Freeman and J.C. Posey, Jr., Dyes and Pigments, **20**(3), 171(1992).
14. H. S. Freeman, M. E. Mason, and J. Lye, Dyes and Pigments, 42**, 53** (1999).
15. L. C. Edwards, "A Study of the Phototostability of Disperse-dyed Poly(ethylene terephthalate Films", Unpublished Masters thesis, North Carolina State University at Raleigh, 1993.
16. N. Berthelon, "The Contribution of PET to the Photodegradation of Disperse Dyes", Unpublished Masters thesis, North Carolina State University at Raleigh, 1998.
17. N. Berthelon and H. S. Freeman, The Contribution of PET to the "Photodegradation of Disperse Dyes", Proceedings of Color Science 98 Conference, Harrogate, England, 1998, pp. 135-140, 1999.