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Light Stability and Flash Photolysis of Azo Dyes in Epoxy Resins

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SUMMARY

The photofading of three azo dyes is examined in various epoxy resin films and the data compared with their photochemical behaviour on flash photolysis in solutions of the resin components. The rate of photofading is found to be mainly dependent upon the structure of the amine hardener and the results are correlated with hydrazyl radical production on solution flash photolysis. Evidence is presented to show that photoreduction is the most important primary photochemical process for azo dyes in epoxy resin films.

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1. INTRODUCTION

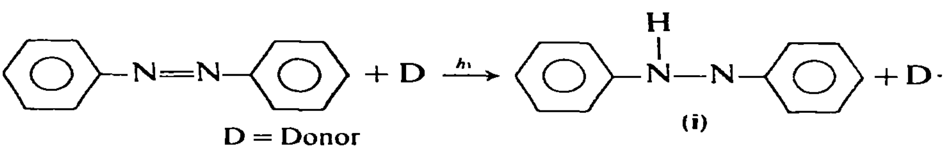
Flash photolysis techniques have been widely applied for studying the photoprocesses of dyes in polymeric media.[1,2] In these studies transient absorption spectra in model solvent systems have been directly related to the light stability of the dyes in polymer films and fabric. Most of the earlier work centred on anthraquinone dyes in nylon and polyester fabric. More recently we have been investigating the photoprocesses of dyes in epoxy resin films based on bisphenol A.[3] These are of interest for the application of dyed epoxy resins in museum conservation work where stability to light exposure is important.[4]

In our earlier work with anthraquinone dyes we found they underwent reductive fading in epoxy resins to give the corresponding, well established, hydroquinone products.[3] This has also been confirmed recently using both conventional and laser flash photolysis [5] Here correlations were obtained between radical transient absorption spectra of the dyes in solutions containing various percentages of epoxy resin components and their light stability in cured resin films.

In view of these findings we have extended our work to cover the important class of azo dyes A relationship between azo dye light stability and transient absorption spectra has not previously been sought

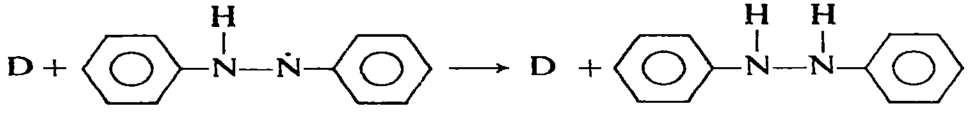
Arylazo dyes are known to undergo direct and indirect photoreduction[6] [7] by hydrogen atom abstraction by the photoexcited state of the dye, from the solvent in the former case, and from the excited state of the reducing agent in the latter.

In 1949 Blaisdell[6] detected the product of photoreduction of azobenzene which was later confirmed by Hashimoto and Kano [8] Van Beek and coworkers[9] [10] then proposed a mechanism for the photoreduction of several azo dyes Only the first stage of this mechanism is of importance in this study, being hydrogen atom abstraction from a suitable donor molecule to give the product (i), a hydrazyl radical



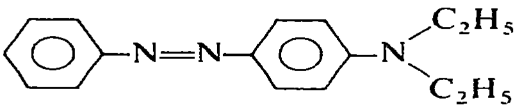
(1)

Van Beek *et al*[9] have used flash photolysis and rapid flow measurements to detect the presence of the transient (i) and with ESR[11] spectroscopy they confirmed its structure. The donors used were DL-mandelic acid in aqueous solution and acetone in ethanol. The hydrazyl radical (i) will react further by hydrogen atom abstraction to give the hydrazo product:

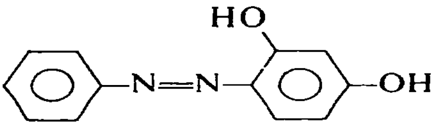

(2)

In this paper we have examined the photofading of the following three azo dyes in various epoxy resin films and compared this with their transient absorption spectra in solution:

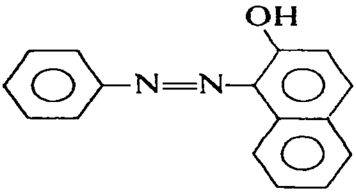
(**I**) 4-Diethylaminoazobenzene



(**II**) 2,4-Dihydroxyazobenzene



(**III**) Phenylazo-2-hydroxynaphthalene

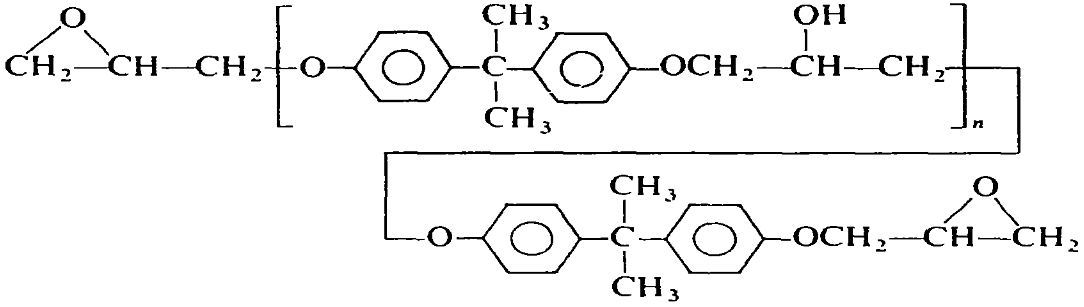


These dyes were chosen for study since they are commercially available and relatively simple in structure, and the photochemistry of related structures is reasonably well understood.[7-11] This enabled an easier consideration of the interactions between the dyes and epoxy resin substrates.

2. EXPERIMENTAL

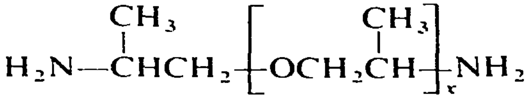
2.1. Materials

The epoxy resins, AY105 and TS600, are diglycidyl ethers of bisphenol A (**IV**) and were supplied by Ciba-Geigy (Plastics and Additives), Cambridge, Great Britain, and Thermoset Plastics Inc., Indiana, USA, respectively



(**IV** $n = 0$-1 depending on end use of resin)

The amine hardeners, XD716 and AB-B, are both polymeric types based on polyoxypropylene tri- and di-amine, respectively. Their corresponding suppliers were as for AY105 above and Ablestick Laboratories, California, USA The TS64 hardener is a diamine of the structure **V** and was supplied by Thermoset Plastics Inc. as above.



$$H_2N{-}CH(CH_3)CH_2{-}[OCH_2CH(CH_3)]_x{-}NH_2$$

(**V**, $x = 2$-3)

None of the resins or hardeners contained any commercial additives except that TS64 contained a few ppm of *p*-cresol. The materials were found to be satisfactory for our purposes and contained no major impurities likely to interfere in this investigation This was confirmed by NMR and mass spectrometry.

The dyes were dissolved in the mixed resin components (see earlier papers for mixing proportions)[3-5] by trituration with the viscous media in a mortar. The dyed resins were then cast into thin films (*ca.* 300 μm thick) between sheets of polyethylene. Glass sheets and spacers were used to provide an even thickness (variation of ±20 μm) Dye concentrations were approximately 10^{-4}M and the films were cured in 48 h.

The two dyes phenylazo-2-hydroxynaphthalene and 2,4-dihydroxyazobenzene were supplied by Bayer Dyestuffs, UK, under the commerical names of Ceres Orange R and Ceres Orange G and 4-diethylaminoazobenzene was supplied by L. B. Holliday Co. Ltd, UK, under the commercial name Fast Oil Yellow 64403.

The resin and hardeners were used as supplied and the dyes were purified on a silica column using chloroform as eluent followed by recrystallisation from ethanol.

Azobenzene was purchased from BDH Chemicals and was recrystallised twice from ethanol.

2.2. Photofading

Fading curves were produced by periodically monitoring the ultraviolet/visible absorption spectra of the dyes with a Perkin Elmer 554 spectrophotometer. Absorption changes were recorded at the wavelength of maximum absorption for each dye. Normalised absorption was then plotted against irradiation time to produce the fading curves. Resin films were exposed in in a Microscal unit (Microscal Ltd, London) under air and nitrogen utilising a 500 W high pressure mercury/tungsten source (λ values >300 nm, RH ambient; 50 °C) Films were purged with nitrogen for 1 h beforehand Any trapped O_2 in the films is expected to be consumed in the early stages of exposure

2.3. Flash photolysis

Conventional μs flash photolysis equipment was employed utilising two high energy xenon filled flash lamps at an operating voltage of 10 kV. All solutions were deoxygenated with oxygen-free nitrogen (<5 ppm O_2).

3. RESULTS AND DISCUSSION

3.1. Photofading behaviour in epoxy resin films

The relative rates of photofading of the three dyes in various epoxy resin films are compared in Figs 1–6 for aerobic and anaerobic conditions. These results show two important features. First, the photofading rates of two of the dyes show no appreciable difference whether irradiated in air or nitrogen. This is apparent in all resin films for **(III)** and **(I)**, but for **(II)**

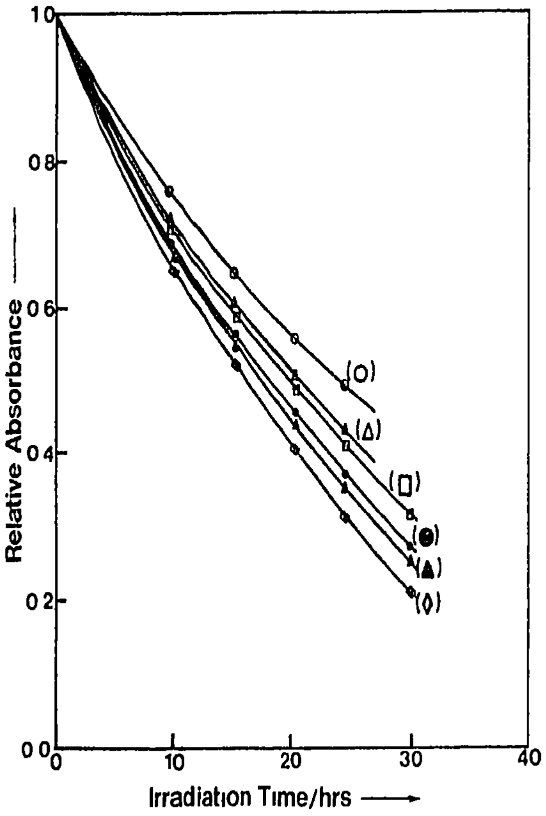


Fig. 1. Relative aerobic photofading curves for phenylazo-2-hydroxynaphthalene in epoxy resin films (~10^{-4}M) (300 μm thick) ●, AY105/AB-B, ○, AY105/TS64, △, AY105/XD716, □, TS600/TS64, ◇, TS600/XD716, ▲, TS600/AB-B

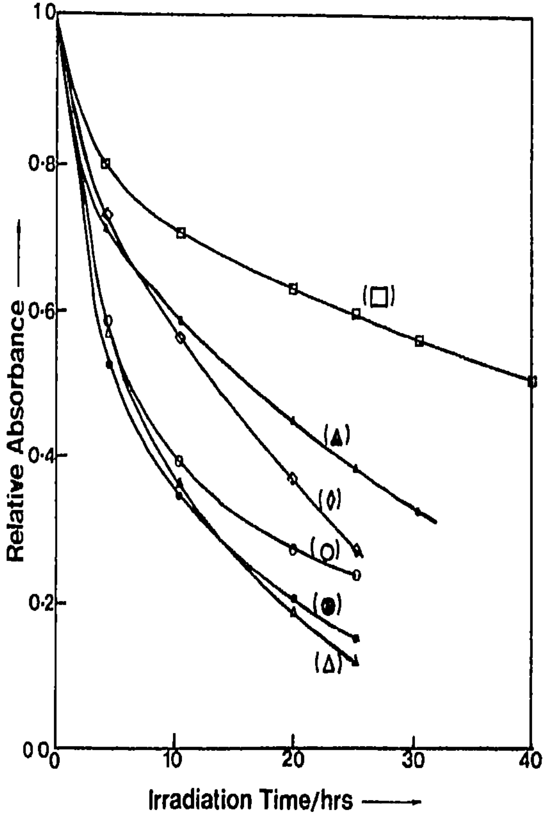


Fig. 2. Relative anaerobic photofading curves for phenylazo-2-hydroxynaphthalene in epoxy resin films (~10^{-4}M) (300 μm thick) symbols as in Fig 1

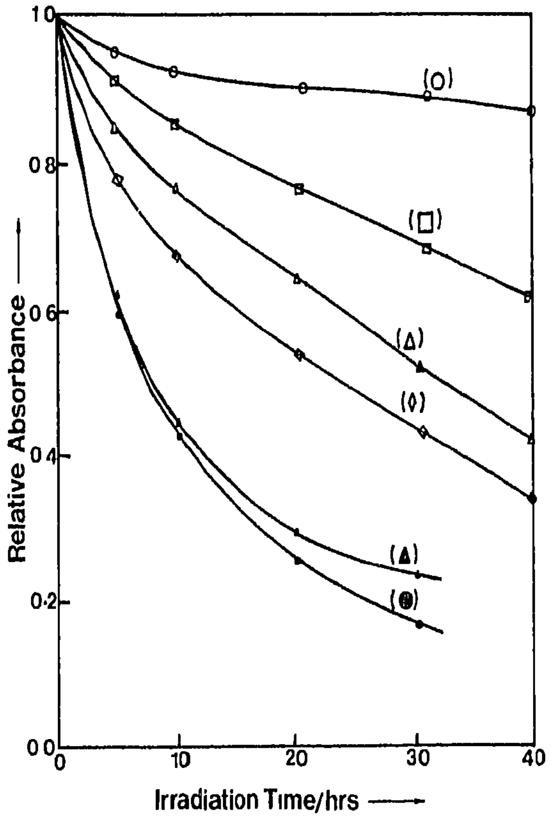


Fig. 3. Relative aerobic photofading curves for 4-diethylaminoazobenzene in epoxy resin films (~10^{-4}M) (300 μm thick) symbols as in Fig 1

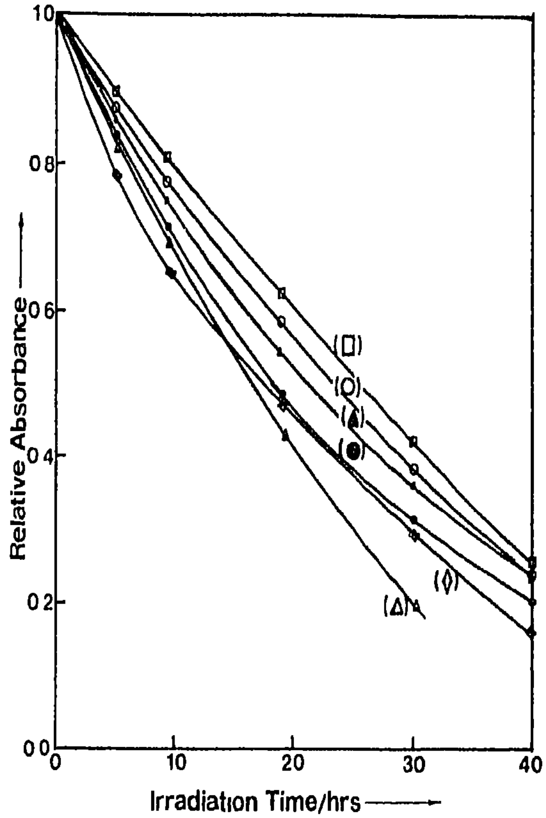


Fig. 4. Relative anaerobic photofading curves for 4-diethylaminoazobenzene in epoxy resin films (~10^{-4}M) (300 μm thick) symbols as in Fig 1

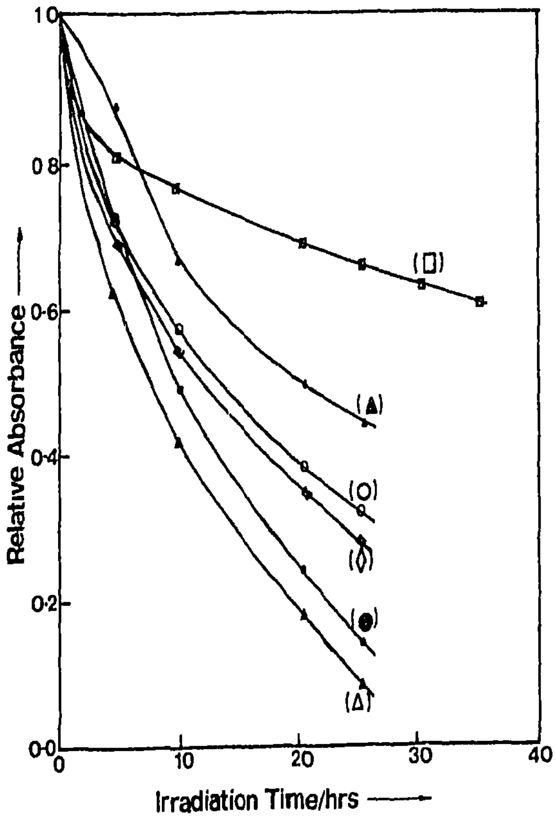


Fig. 5. Relative aerobic photofading curves for 2,4-dihydroxyazobenzene epoxy resin films (~ 10^{-4} M) (300 μm thick) symbols as in Fig 1

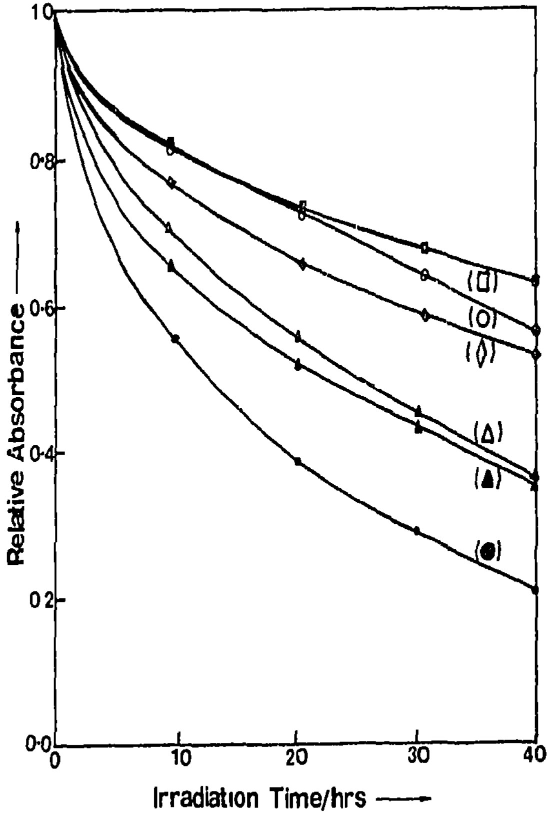


Fig. 6. Relative anaerobic photofading curves for 2,4-dihydroxyazobenzene in epoxy resin films (~ 10^{-4} M) (300 μm thick) symbols as in Fig 1

there were a number of differences in fading rates. These differences, however, were variable and inconsistent and in general it may be concluded with certainty that singlet oxygen is unimportant in the photofading of azo dyes in epoxy resin films. In support of this conclusion we also found that the addition of a singlet oxygen scavenger, DABCO,[1,3,7] has no effect on the fading rates of all three dyes in the resin films. In fact, as a further point of interest, we examined the effect of a number of commercial light stabilisers and antioxidants, such as nickel chelates, ultraviolet absorbers and hindered phenols/phosphites at various concentrations up to 0·5% w/w, and none of them had any influence on the fading rates of the three dyes studied.

The second feature, and one that is apparent from all the Figures, is that the photofading rates are highly dependent on the epoxy resin composition Since the resins AY105 and TS600 are structurally similar, the fading rates would be expected to be unaffected in the presence of the same hardener. However, as seen from all the fading curves, the nature of the resin itself does have an effect, particularly for dyes (**I**) (Figs 3 and 4) and (**II**) (Figs 5 and 6), where, in general, AY105 is more active than TS600 in accelerating the fading rate. Of more importance, however, is the nature of the amine hardener. For dyes (**III**) (Figs 1 and 2) and (**I**) (Figs 3 and 4) the activity of the hardeners, and hence fading rates, decrease in the order XD716 > AB-B > TS64 whereas for dye (**II**) (Figs 5 and 6) the activity is AB-B > XD716 > TS64 The hardener TS64 appears to offer a much better degree of stability to the dyes, particularly when formulated with the TS600 resin component. Similar results were observed earlier with anthraquinone dyes[3,5] where we found the photofading rates of the dyes to be dependent upon the functionality of the amine hardener. This would also appear to be the case here for azo dyes where the lowest functionality diamine hardener, TS64, imparts the greatest stability to the dyes.

The highly reductive nature of the epoxy resin components is seen from the next section on flash photolysis where, in general, the photofading rates of the dyes in films are correlated with their transient absorption intensities due to hydrazyl radical production in solutions of the resin components.

3.2. Flash photolysis behaviour in solution

End-of-pulse transient absorption spectra of the dyes in the absence and presence of various epoxy resin components (5% w/w) in toluene solution

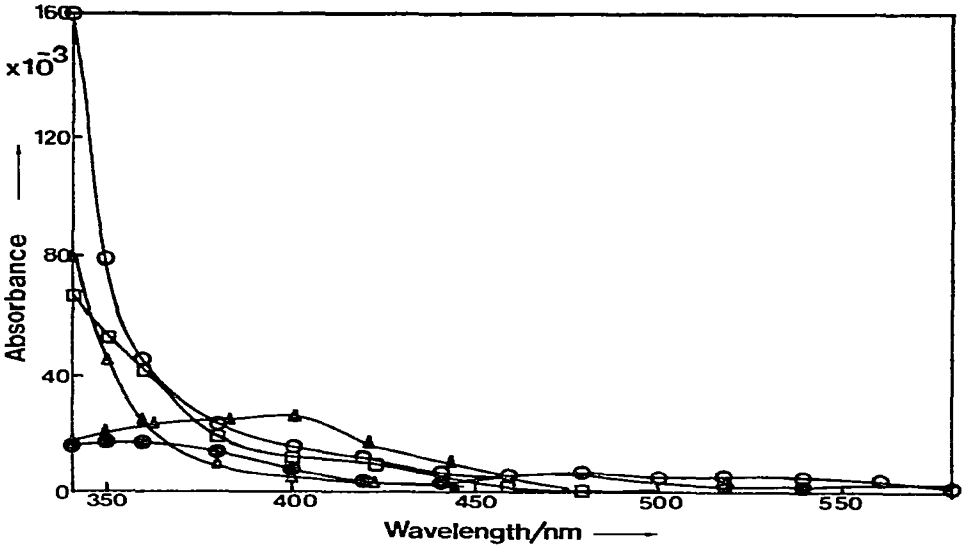


Fig. 7. End-of-pulse transient absorption spectra produced on flash photolysis of 2,4-dihydroxyazobenzene in nitrogen-saturated toluene (~ 10^{-5}M) containing ●, no resin components, or 5% w/w of ▲, AY 105, ○, XD716, △, TS64 □, AB-B

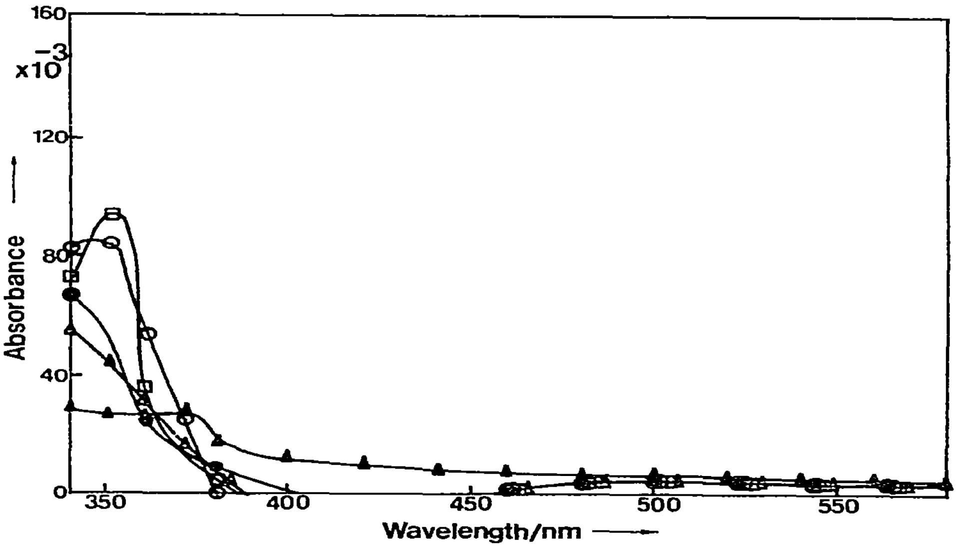


Fig. 8. End-of-pulse transient absorption spectra produced on flash photolysis of 4-diethylaminoazobenzene in nitrogen-saturated toluene (~ 10^{-5}M) symbols as in Fig 7

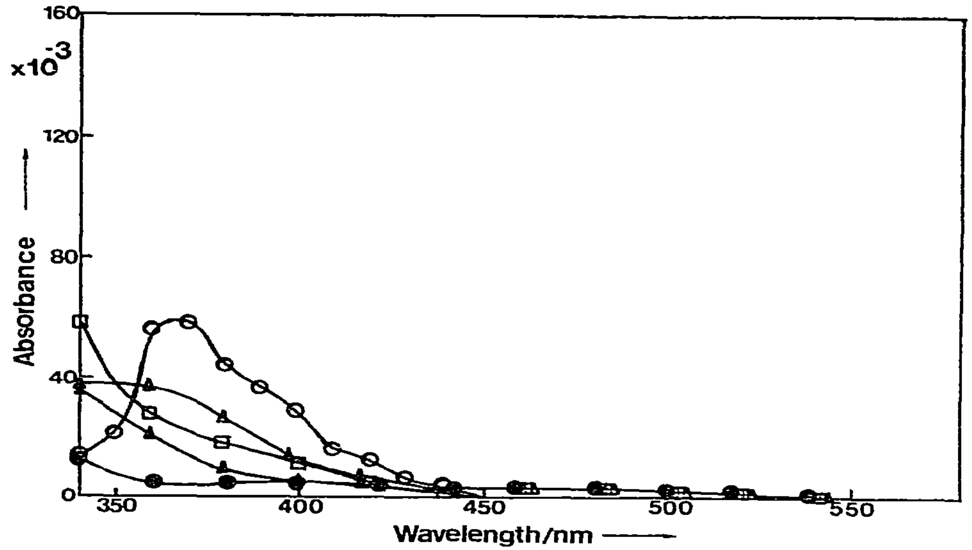


Fig. 9. End-of-pulse transient absorption spectra produced on flash photolysis of phenylazo-2-hydroxynaphthalene in nitrogen-saturated toluene (~ 10^{-5}M) symbols as in Fig 7

are shown in Figs 7–9. Toluene was found to be the most appropriate solvent here for all the epoxy resin components since it gave an optically clear solution. It also absorbs most of the u v. wavelengths <300 nm to give a spectral excitation which simulates closely the fading conditions of the dyes in the films

Unfortunately toluene is not the most suitable solvent for observing well-resolved transient absorption spectra, as may be seen from the figures. The transient absorption spectra of all three dyes exhibit broad maxima below 400 nm with a weaker band at about 475–500 nm The presence of all the resin components examined enhances the transient absorption, the most effective being the amine hardeners, particularly XD716 and AB-B.

No transient absorptions were observed from the resin components.

To identify the transient absorption spectra of the dyes, flash photolysis studies were carried out in an ethanol/acetone mixture (99:1, v/v) for one of them, namely (III), and its spectrum was compared with that produced for azobenzene. The latter, on photoreduction, is known to produce a hydrazyl radical whereas dye (III) has also been reported to give a naphthoxyl radical. The transient spectra are compared

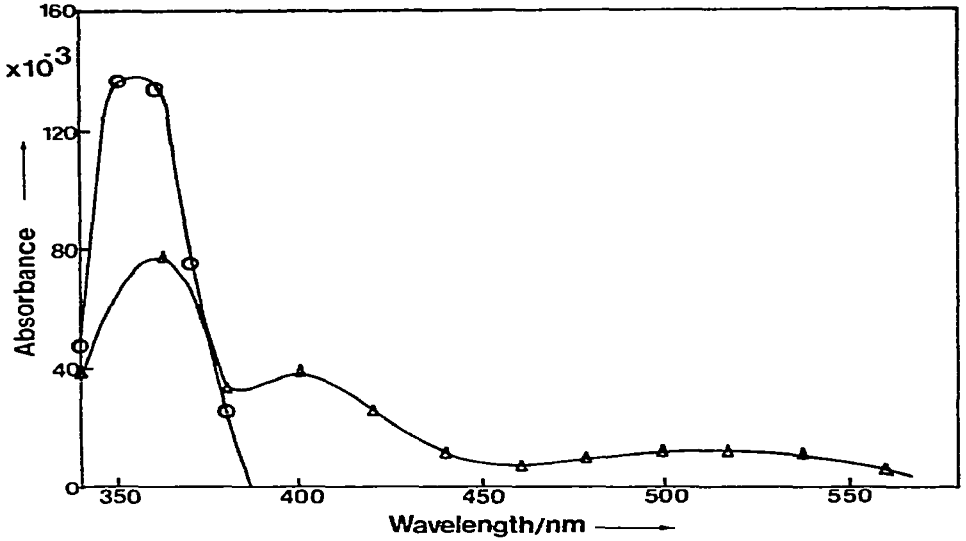
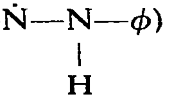


Fig. 10. End-of-pulse transient absorption spectra produced in flash photolysis of ○, phenylazo-2-hydroxynaphthalene △, azobenzene in nitrogen-saturated ethanol/acetone (99 1 v/v, ~10^{-5}M)

in Fig 10, where it is seen that both spectra have intense maxima at 360 nm Azobenzene also gives weaker bands at 400 and 500 nm. The absence of these bands for dye (III) is probably due to the stronger absorption by the dye in this region of the spectrum compared with azobenzene The absence of any other transient absorption by dye (III) clearly indicates that there is no interference from any other possible radical intermediates The spectra shown in Fig. 10 are, therefore, tentatively assigned to the corresponding hydrazyl radical



$$(\phi\text{—}\dot{\text{N}}\text{—N—}\phi)$$
$$\text{with H on the second N}$$

formed through hydrogen atom abstraction from the solvent. The radical is capable of migrating between the two nitrogen atoms and this can affect the nature of the spectrum The assignment is partly confirmed by the fact that the transient intensity is significantly greater in a strongly hydrogen atom donating system (ethanol/acetone) (Fig. 10) than in a non-reducing solvent, toluene (Fig 9).

TABLE 1

Transient Absorption Intensity ($\times 10^3$) at 360 nm on Flash Photolysis of Phenylazo-2-hydroxynaphthalene in Toluene Containing Epoxy Resin Components

Resin/hardener	*Transient absorption intensity* $\times 10^3$ *Concentration* (% *v/v*)		
	1 0	*3 0*	*5 0*
AY105	17 42	14 72	22 82
AB-B	16 44	26 87	25 77
XD716	19 70	67 42	55 05
TS64	21 12	16 20	34·45

Thus all three dyes are capable of undergoing photoreduction to give a hydrazyl radical and this process is examined more quantitatively for increasing concentrations of AY105 resin and XD716, AB-B and TS64 hardeners in Tables 1–3. Here transient absorption intensities at 360 nm for the dye hydrazyl radicals are tabulated and, as seen from the discussion below, can be related to the fading rates of the dyes in the corresponding resin films.

The transient absorption intensities for the three dyes in Tables 1–3 show two interesting features

The first, which applies to all three dyes, is that increasing the concentration of the resin AY105 from 1 0 to 5 % w/w has no significant

TABLE 2

Transient Absorption Intensity ($\times 10^3$) at 360 nm on Flash Photolysis of 2,4-Dihydroxyazobenzene in Toluene Containing Epoxy Resin Components

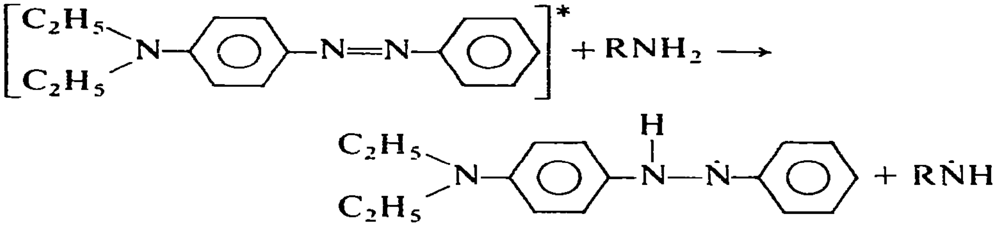
Resin/hardener	*Transient absorption intensity* $\times 10^3$ *Concentration* (% *w/v*)		
	1 0	*3 0*	*5 0*
AY105	24 71	24 52	23 62
AB-B	42 60	65 50	55·52
XD716	45 76	68 00	44 52
TS64	26 87	40 29	23 58

TABLE 3
Transient Absorption Intensity ($\times 10^3$) at 360 nm on Flash Photolysis of 4-Diethylaminoazobenzene in Toluene Containing Epoxy Resin Components

Resin/hardener	*Transient absorption intensity × 10^3*		
	Concentration (% w/w)		
	1 0	*3 0*	*5 0*
AY105	28 49	36 21	27 58
AB-B	24 82	39 58	35 40
XD716	33 50	48 22	51 33
TS64	23 17	30 18	31 52

effect on hydrazyl radical production For the amine hardeners, on the other hand, there is generally a gradual increase in transient absorption intensity with increasing concentration. The second is the correlation between transient intensity and dye fading rate In Table 1 the most reductive hardener is XD716: this is consistent with its activity in accelerating the photofading of dye PAHN compared with the other two hardeners The difference in photofading rates for dye (**III**) in resins containing AB-B and TS64 is only small and this is reflected by the poor correlation over the concentration range studied. For dye (**II**) in Table 2 there appears to be a maximum in transient absorption intensity at 3 0% w/w of hardener. Here the most active hardeners, AB-B and XD716, on photofading give the more intense transient absorptions whilst the least active, TS64, gives the lowest transient absorption. In fact, at the 5% w/w concentration the activities of the amine hardeners decrease in the order AB-B > XD716 > TS64 which correlates exactly with their activities on the photofading of the dye In Table 3 there is a correlation, over the three concentration ranges, between the transient absorption intensities and the photofading rates of the dye (**I**) in epoxy resins Here the order of hydrazyl radical production is XD716 > AB-B > TS64, this compares very favourably with the activity of the amine hardeners in enhancing the photofading of the dye in solid films.

It is evident from the results that there is a reasonable correlation between the ease of photoreduction of the dyes in solutions of the resin components and their rates of photofading in resin films. Thus, the photoexcited dyes are capable of abstracting a hydrogen atom from the resin environment to give a hydrazyl radical. For (**I**) and an amine we have.



The hydrazyl radical will then react further as shown in reaction (2) above. The spectral changes of the three dyes on photofading in the epoxy resin films showed no evidence for product formation.

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