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Photofading of Anthraquinone Disperse Dyes in Epoxy Resin Films: Photoreduction, Energy Transfer and Photostabilisation Processes

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SUMMARY

*The photofading of three anthraquinone disperse dyes, 1- and 2-piperidino- and 1-hydroxy-4-(*p*-toluidino)-anthraquinone has been examined in a number of epoxy resin systems using UV–visible absorption spectroscopy. Compared with a relatively inactive polymer system such as cellulose triacetate the epoxy resins accelerate photofading through a reduction mechanism, which is, in turn, dependent on the structure of the dye and functionality of the hardener. A number of stabiliser systems are examined on the fading rate of one of the dyes and one of them, an* N*-oxy radical, is highly effective in inhibiting photoreduction. A regenerative mechanism involving the hydroxylamine is discussed. Evidence for a triplet-to-singlet energy transfer process from the polymer to the 2-piperidino derivative is also presented.*

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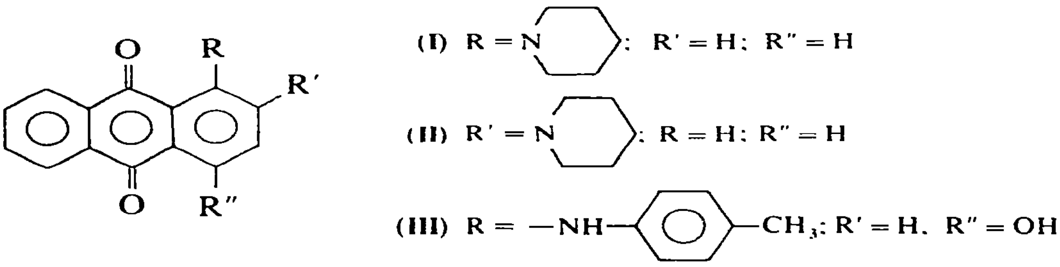
1. INTRODUCTION

The effect of light on dyed and pigmented epoxy resin systems is an important technological problem since for many applications, such as museum conservation, stability to prolonged sunlight exposure is essential.[1,2] This applies to both the dye/pigment and the resin. Unfortunately, epoxy resins deteriorate on exposure to sunlight and undergo extensive chain scission, cross-linking and yellowing.[3-6] In addition to this is the ability of epoxy resins to sensitise the photofading of dyestuffs.[2] For example, many commercial dyes which normally have high light stability in, say, polyesters[7] have poor light stability in epoxy resins. This can be a problem in stained glass restoration where colour matching is important.

In a recent paper[8] we examined the spectroscopic properties of a number of commercial epoxy resin systems to elucidate the nature of the species responsible for their sensitivity to sunlight exposure. The results indicated that the Bisphenol A unit (diphenylol propane) is responsible for light absorption in this region of the spectrum and subsequent photoyellowing. The complex interactions involved in dyed epoxy resins, however, remain unresolved. To this end we have examined the photofading behaviour of three anthraquinone disperse dyes, structures **I–III**, in a number of epoxy resin systems.



The first two dyes were selected for study since their basic photochemistry is reasonably well established, particularly with regard to their mechanisms and products.[7,9-15] This allows an easier understanding of the complex interactions between the dye and the resin. The third dye was selected for comparison purposes only. The fluorescence property of dye **II**[11,15] enables us to study the electron-donating property of the amine hardeners through Stern–Volmer quenching[15,16] and the possible involvement of triplet–singlet resonance energy transfer from the polymer to the dye.[17] Finally, the effect of a number of stabilisers has been examined on the photofading rate of dye **I** in order to overcome the problem of enhanced fading in epoxy resins.

2. EXPERIMENTAL

2.1. Materials

The resins and hardeners used in this study together with their formulae, mixing proportions and manufacturers are given in Table 1. Hexamethylene diamine was purchased from Hopkins and Williams Ltd, UK. The cellulose triacetate (~ 100 μm thick) was obtained from Bexford Ltd, UK. The functionalities of the hardeners were obtained using vapour pressure osmometry and mass spectrometry followed by titration with standard acid.

TABLE 1
Epoxy Resin Systems Used

Epoxy systems	*Constituents*	*Mixing proportions*
Araldite AY 105[a] resin	Bisphenol A diglycidyl ether	100
Thermoset 600 resin[b]	Bisphenol A diglycidyl ether	100
XD716 hardener[a]	$[\text{—CH(NH}_2\text{)C(CH}_3\text{)(NH}_2\text{)CH(NH}_2\text{)—O—}]_x$	37
Ablebond 342–1[c] hardener	Polyoxypropylene diamine	32

[a] Ciba-Geigy (Plastics and Additives) Company, Cambridge, UK.
[b] Thermoset Plastics Inc., Indiana, USA.
[c] Ablestik Laboratories, California, USA.

The dyes, 1- and 2-piperidinoanthraquinone and 1-hydroxy-4-(*p*-toluidino) anthraquinone, were supplied by the Fine Chemicals Service of ICI Ltd, Manchester, UK. All the dyes were purified on an alumina column using chloroform as eluent and ethanol for recrystallisation.

The stabilisers used in this study together with their formulae and manufacturers are listed in Table 2.

The dyes and stabilisers (0·1 % w/w) were blended into the resins before curing. Films ~400 μm thick were obtained by curing the resins between sheets of polyethylene for 1 week. Dye concentrations in the resins were about 10^{-4}M.

TABLE 2
Stabiliser Systems Used

Stabiliser	*Formula*	*Supplier*
Tinuvin 770	Bis[2,2,6,6-tetramethyl-4-piperidinyl] sebacate	Ciba-Geigy Corp., Switzerland
—	4-hydroxy-2,2,6,6-tetramethylpiperidino-*N*-oxy	Eastman Kodak Company, USA
NiDBDTC	Nickel dibutyldithiocarbamate	E. I. Dupont De Nemours Inc., USA
Cyasorb UV 531	2-hydroxy-4-*n*-octoxybenzophenone	American Cyanamid Company, USA
—	Tetracyanoethylene	Aldrich Chemical Company, USA
Negopex B	Nickel bis(*syn*-undecyl-2-hydroxy-4/5-methylphenylketoxime)	ICI Ltd, UK

2.2. Spectroscopic measurements

Ultraviolet–visible absorption spectra were recorded using a Perkin–Elmer Model 554 spectrometer equipped with a microprocessor for recording first ($dA/d\lambda$) and second ($d^2A/d\lambda^2$) order spectra.

Fluorescence spectra were recorded at room temperature (300 K) using a Baird Atomic Model 100E Fluorispec. Phosphorescence spectra were recorded at 77 K (liquid nitrogen) using an Aminco–Bowman phosphorimeter.

2.3. Irradiation

The polymer films were exposed in a Microscal unit (Microscal Ltd, London, UK) under air and nitrogen utilising a 500 W high-pressure mercury/tungsten source (wavelengths > 300 nm).

3. RESULTS AND DISCUSSION

3.1. Rates of photofading

The rates of photofading of all three dyes **I–III** in two different epoxy resin formulations are compared in Fig. 1 with their fading rates in

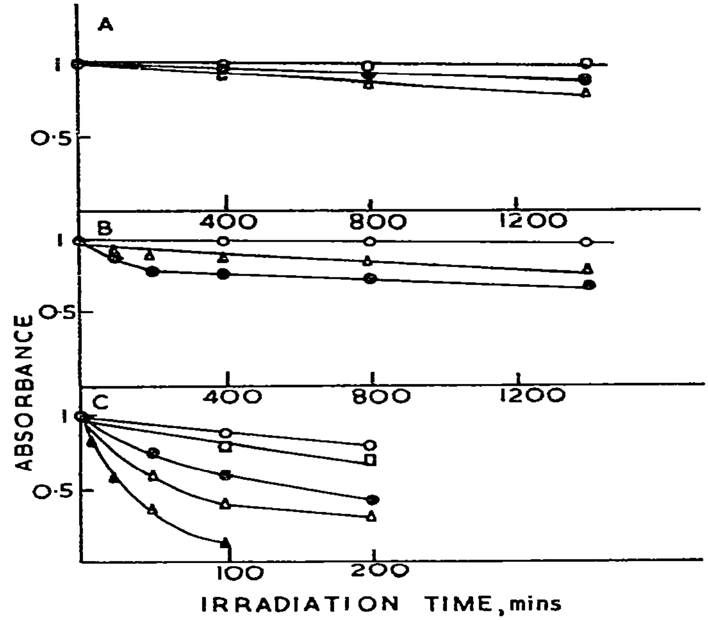


Fig. 1. Decrease in absorbance versus irradiation times in the Microscal unit for (A) 1-hydroxy-4-(*p*-toluidino) anthraquinone, (B) 1-piperidinoanthraquinone and (C) 2-piperidinoanthraquinone in (○) cellulose triacetate in air, (□) cellulose triacetate in nitrogen, (●) epoxy resin AY105/Ablebond 342-1 in air, (△) epoxy resin AY105/XD716 in air and (▲) epoxy resin AY105/XD716 in nitrogen.

cellulose triacetate. It is seen that all the dyes fade appreciably faster in the epoxy resins under aerobic conditions than in cellulose triacetate. The nature of the amine hardener is also important. For example, in the case of dyes **II** and **III** the hardener XD 716, with a functionality of 15, induces faster fading than the corresponding difunctional Ablebond hardener. The reverse situation is observed however in the case of dye **I**. The fading rates of dyes **I** and **III** under anaerobic conditions were found to be unaltered whereas the rates of dye **II** were faster. An example of this effect is also shown in the figure for one of the resin systems and cellulose triacetate. Clearly, oxygen is quenching the excited triplet state of this dye. The nature of the resin component was found to have little effect on the fading rates of the dyes. This is not surprising since they have the same structures. The structure of the amine hardener is evidently more important, suggesting the possible involvement of an electron transfer process in fading.

3.2. Stern–Volmer quenching

One of the dyes, 2-piperidinoanthraquinone, is believed to fade through an electron transfer process[11,15] and the evidence for this was based on the observation of a correlation between quenching efficiency of the dye fluorescence and the ionisation potential of a number of amine systems. We carried out a similar experiment for two of the amine hardeners and hexamethylenediamine. The results are shown in Fig. 2, where it is seen that quenching efficiency increases with an increase in the functionality of the hardener. Thus, from these results it would appear that amine hardeners with a high functionality are more likely to induce fading through an electron transfer process. However, the involvement of other processes cannot be ruled out, particularly in view of the fact that epoxy resins contain other active constituents, evidence for which is provided by the spectral results below.

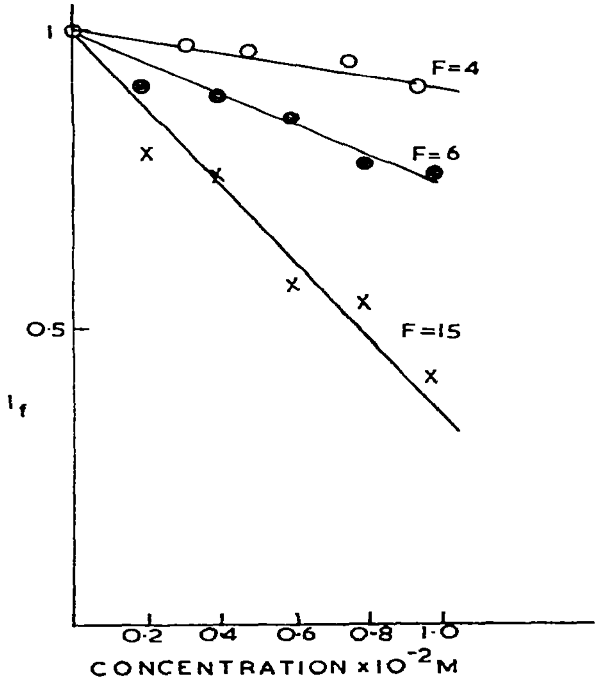


Fig. 2. Stern–Volmer quenching plots on the fluorescence emission of 2-piperidinoanthraquinone by (○) hexamethylenediamine, (●) Ablebond 342-1 and (×) XD716 in chloroform (F = functionality).

3.3. Spectral changes

In the presence of oxygen the fading was complex and there was no evidence of any definite product formation. However, under anaerobic conditions product formation was observed for both the dyes **I** and **III**. Thus, the spectral changes for the 1-piperidino derivative in an epoxy resin system are shown in Fig. 3. It is seen that fading occurs directly to give a product absorbing in the region 350–450 nm with an isobestic point at about 460 nm. The absorption spectrum of the product is seen to match closely that of the hydroquinone form of the dye produced by reduction with zinc and hydrochloric acid in ethanol (50:50 v/v).[12,13] A second order derivative spectrum of the product indicates the presence of maxima at 384, 394 and 414 nm. For a second order spectrum all minima are either absorption maxima or vibrational maxima on a main

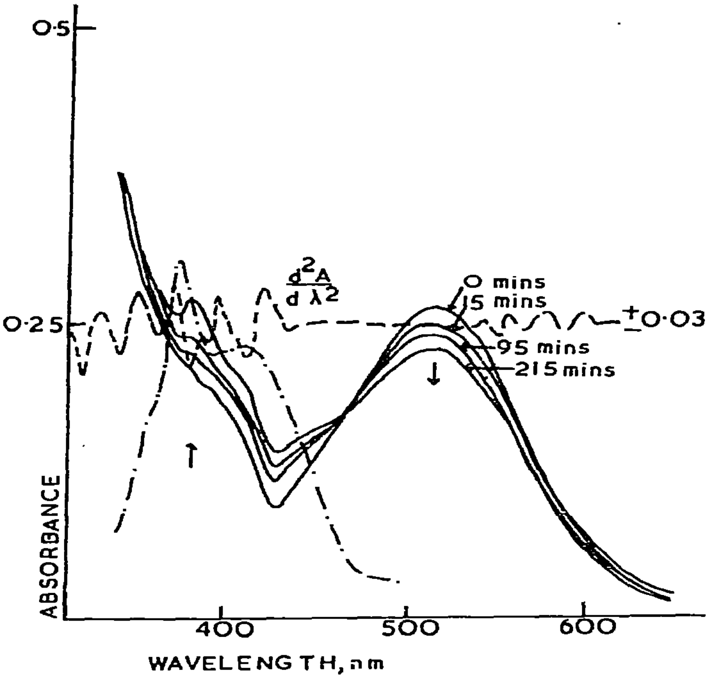


Fig. 3. Changes in the absorption spectrum of 1-piperidinoanthraquinone in epoxy resin AY105/Ablebond 342–1 during irradiation in the Microscal unit under nitrogen (———). – – –, Second order derivative spectrum after 215 min of irradiation. — · — · —, Absorption spectrum of the hydroquinone produced after reduction of the dye with Zn hydrochloric acid in ethanol.

absorption band. In cellulose triacetate no product formation was observed and fading was significantly slower over the same period of time. The formation of the hydroquinone is well known and occurs through hydrogen atom abstraction by the excited triplet state of the dye:[14]

$$A \xrightarrow{h\nu} A^1 \xrightarrow{\text{ISC}} A^3 \qquad (1)$$

Intersystem
crossing

$$A^3 + P\text{—}H \longrightarrow AH\cdot + P\cdot \qquad (2)$$

$$2AH\cdot \longrightarrow A + AH_2 \text{ (hydroquinone)} \qquad (3)$$

or

$$AH\cdot + P\text{—}H \longrightarrow AH_2 + P\cdot \qquad (4)$$

Reaction (3) is a disproportionation process involving two semiquinone radicals.

The spectral changes for 1-hydroxy-4-(*p*-toluidino) anthraquinone in an epoxy resin medium are shown in Fig. 4. In this case it is seen that product formation occurs in the spectral region 400–480 nm with an isobestic point at 500 nm. The absorption spectrum of the product matches closely that of the anthrone form of the dye produced by

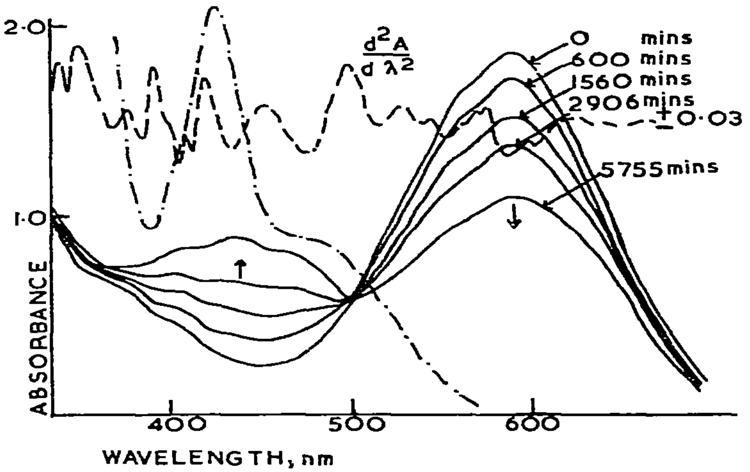
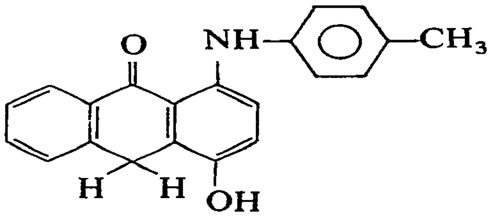


Fig. 4. Changes in the absorption spectrum of 1-aminotoluidinoanthraquinone in epoxy resin AY105/XD716 during irradiation in the Microscal unit under nitrogen (——). – – –, Second order derivative spectrum after 5755 min of irradiation. —·—·—, Absorption spectrum of the anthrone form produced after reduction of the dye with alkaline sodium dithionite.

reduction in alkaline sodium dithionite.[18] The second order derivative spectrum indicates main absorption maxima at 394, 404, 414, 434 and 476 nm. In cellulose triacetate again no product formation was observed and fading was considerably slower. It would appear that for this dye photoreduction is different, giving the anthrone of structure **IV**:



(IV)

According to Bradley and Masey[18] some 1-substituted anthraquinone dyes form the anthrone by this process although our product **IV** was unstable and difficult to isolate.

Spectral changes for the 2-piperidino derivative are shown in Fig. 5 for an epoxy resin. There is no evidence of any product formation in this system and fading is much faster in cellulose triacetate. In this case fading must involve electron transfer to give the radical anion ($A^{\cdot -}$). The strong reductive nature of the epoxy resin environment, as evidenced above, certainly suggests that a reductive mechanism involving electron transfer is likely although the involvement of singlet oxygen cannot, of course, be ruled out. This aspect is receiving further detailed study. All the above spectral changes were consistent from one resin type to another.

3.4. Triplet–singlet resonance energy transfer

One other factor that could contribute to the enhanced fading rate of the dyes in an epoxy resin is the transfer of triplet energy from the polymer to the dye giving a potentially active long-lived singlet excited state.[17] The importance of such a mechanism has been disputed by some workers but their evidence was based on the use of a relatively inactive polyethylene-terephthalate substrate.[19] Excitation of epoxy resins at 290 nm gives phosphorescence emission with a maximum at 440 nm. This emission originates from the Bisphenol A unit in the polymer structure. In the presence of increasing amounts of 2-piperidinoanthraquinone it is seen that the polymer phosphorescence is reduced and a second band with a maximum at 600 nm appears (Fig. 6). This second band matches the normal fluorescence emission of the dye in the polymer indicating the

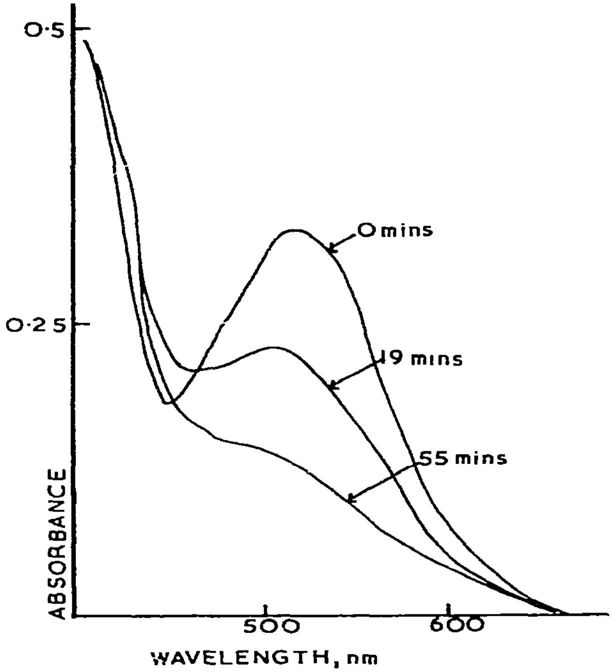


Fig. 5. Changes in the absorption spectrum of 2-piperidinoanthraquinone in epoxy resin AY105/XD716 during irradiation in the Microscal unit under nitrogen.

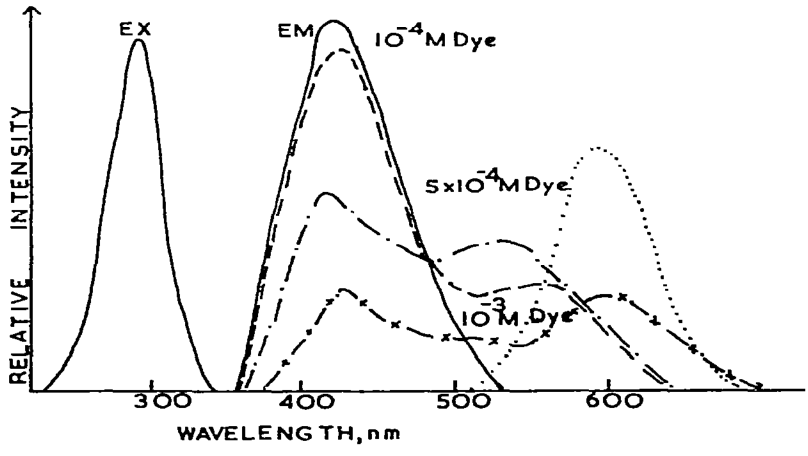


Fig. 6. Phosphorescence emission spectrum of the epoxy resin AY105/XD716 containing (——) no dye, (- - -) 10^{-4} M, (—·—·) 5×10^{-4} M and (—×—) 10^{-3} M 2-piperidinoanthraquinone. ······, Normal dye fluorescence. Excitation wavelength = 290 nm.

involvement of triplet–singlet resonance energy transfer from the polymer to the dye.

3.5. Stabilisation

The influence of a number of stabilisers on the rate of fading of one of the dyes, namely 1-piperidinoanthraquinone, is shown in Fig. 7. It is seen that initially all the stabilisers are effective in inhibiting dye fading. After a period of about 300 min the tetracyanoethylene and Tinuvin 770 accelerate the rate of fading. All the other stabilisers vary significantly in terms of their efficiency, the most effective being the *N*-oxy radical compound.

The stabilising effects are worthy of some detailed discussion since together they each fit into a link within the complex mechanism of the dye fading process. The marked stabilising effect of the *N*-oxy radical is clearly due to its ability to react with the semiquinone radical (AH·) product in mechanism (2) above by reaction (5).

$$>\text{N—O}\cdot + \text{AH}\cdot \longrightarrow >\text{N—OH} + \text{A} \qquad (5)$$

This mechanism involves the formation of a hydroxylamine and regeneration of the dye and has been confirmed in earlier work using flash

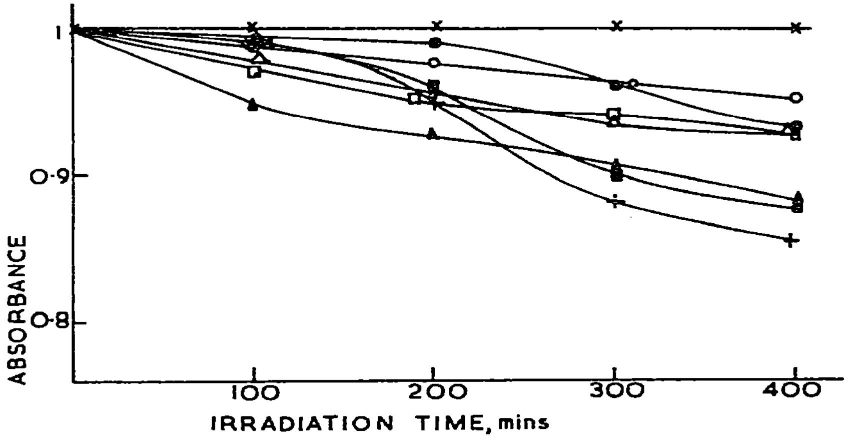
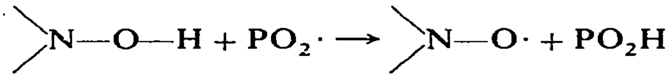


Fig. 7. Decrease in the absorbance of 1-piperidinoanthraquinone in epoxy resin Thermoset 600/XD716 containing (▲) no stabiliser, (○) 0·1% Negopex B, (△) 0·1% DABCO, (□) 0·1% UV531, (●) 0·1% nickel dibutyldithiocarbamate, (×) 0·1% 4-hydroxy-2,2,6,6-tetramethylpiperidino-*N*-oxy, (+) 0·1% Tinuvin 770 and (■) 0·1% tetracyanoethylene during irradiation in the Microscal unit.

photolysis.[20,21] The efficiency of the *N*-oxy radical compounds in photostabilisation is due to the following regeneration process involving peroxy radicals:[20]

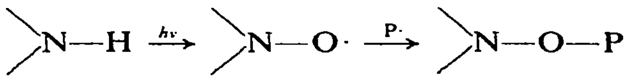


$$\rangle N{-}O{-}H + PO_2\cdot \longrightarrow \rangle N{-}O\cdot + PO_2H \qquad (6)$$

The peroxy radicals are easily formed following reactions (2) and (4) by:

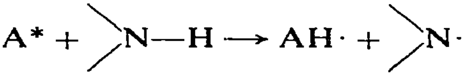
$$P\cdot + O_2 \longrightarrow PO_2\cdot \qquad (7)$$

The initial stabilising effect of Tinuvin 770, a hindered amine, is evidently due to the production of the nitroxyl radical:[20,22]



$$\rangle N{-}H \xrightarrow{h\nu} \rangle N{-}O\cdot \xrightarrow{P\cdot} \rangle N{-}O{-}P \qquad (8)$$

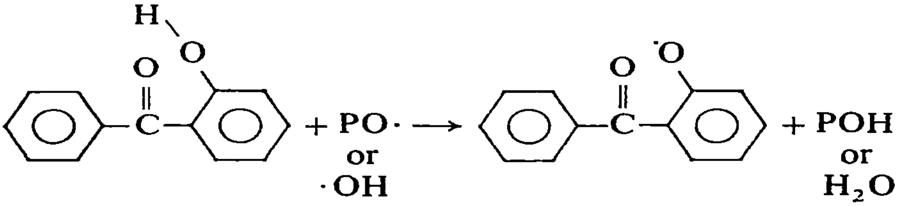
However, the presence of the dye appears to antagonise this process since its efficiency is significantly reduced during the later stages of irradiation, probably through the following hydrogen atom abstraction process:



$$A^* + \rangle N{-}H \longrightarrow AH\cdot + \rangle N\cdot \qquad (9)$$

The tetracyanoethylene, a well-known electron trap, [21,23] also exhibits an initial stabilising effect, suggesting the involvement of an electron transfer process to give the radical anion ($A\cdot^-$). However, the importance of other processes appears to dominate during the later stages of irradiation.

The involvement of hydroperoxides and derived radicals in the fading process is indicated by the stabilising effects of the nickel complexes. Nickel dibutyldithiocarbamate is a well-known hydroperoxide decomposer, as is Negopex B.[24-26] The higher efficiency of Negopex B may be due to its ability to trap radicals such as PO· and ·OH produced in the photolysis of hydroperoxides[25,26] and also to its ability to quench the triplet state of the dye.[27] The 2-hydroxybenzophenone, UV531, is also a stabiliser and has been shown to operate by trapping PO· and ·OH radicals:[28,29]



(10)

This is a sacrificial mechanism and would eventually result in loss of the stabiliser. The screening action of this type of stabiliser is now believed to be unimportant.[6,30]

The stabilising effect of DABCO is interesting since it indicates that singlet oxygen may also be important in dye fading.[31] As mentioned earlier this aspect is receiving further detailed study. However, it should be pointed out that from a comparison of the initial fading curves for DABCO and the nitroxy radical it is evident that hydrogen atom abstraction is the predominant fading mechanism.

4. CONCLUSIONS

Epoxy resins are strong reductive environments and have a deleterious effect on the light stability of anthraquinone disperse dyes. Radical traps appear to be effective in inhibiting the reductive processes.

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