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The influence of singlet oxygen in the fading of carbonless copy paper primary dyes on clays

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Abstract

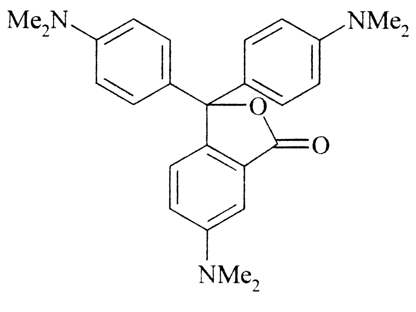
Singlet oxygen was shown to be involved in the mechanism of fading on a clay surface of a series of the triphenylmethane (TPM) dyes used in commercial carbonless copying paper. The dyes adsorbed on clays were found to be singlet oxygen sensitisers and the singlet oxygen produced reacted with the dyes themselves. The rate of fading of a particular dye depended upon the structure of the dyes, fluorans degrading faster than phthalides. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Singlet oxygen; Fading; Carbonless copy paper; Leuco dyes; Clays

1. Introduction

Carbonless copying paper systems are based on the rapid development of a primary leuco dye colour former, which becomes coloured on contact with a coreactant which is often an acid activated montmorillonite clay [1]. Triphenylmethane (TPM) leuco dyes such as Crystal Violet lactone (CVL) **1** are favoured as colour formers because of their low cost and strong developed colour, but unfortunately the intensity of the primary dye fades with time and exposure to light [2]. To offset this fading, a slowly developing secondary dye, for example carbazolyl blue (S-RB), is also included in the system [3].

The irreversible photodegradation reactions of the TPM dyes may be broadly classified as either photo-oxidation or photoreduction processes. Analysis of the stable photoproducts and intermediates suggests three possible pathways for photodecomposition both in solution and on cellulose acetate fibres. These are:



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(a) Dealkylation of the alkylamino groups, which appears to proceed via the *N*-oxide (Scheme 1) [4–13].

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(b) Oxidative cleavage, possibly via singlet oxygen, of the central C-phenyl bond to give benzophenones and phenols [9,10]. The reaction of singlet oxygen ($^1\Delta_gO_2$) with TPM dyes has received considerable attention over the last two decades. TPM dyes, like many other classes of dye, produce singlet oxygen upon photolysis by visible light on cellulose acetate [13]. The photo-degradation of TPM dyes in dichloromethane is accelerated by Methylene Blue (a singlet oxygen sensitiser), but retarded by singlet oxygen quenchers such as β-carotene and zinc(II) and nickel(II) complexes [9]; [10]. On the other hand, fading is only slightly altered by addition of 2,6-di-*t*-butyl-*p*-cresol, a good free radical scavenger [9].

(c) Reduction of an excited state dye cation to a colourless leuco dye form may also be a possible route of fading [4,13,14].

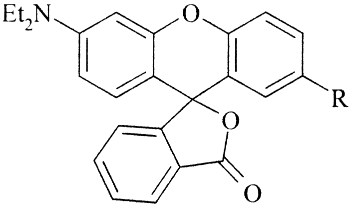
Several different reactions may occur under the same experimental conditions and Scheme 2 shows the fading mechanisms, which appear to occur with Crystal Violet **2** [9,10]. Crystal Violet Lactone **1** itself appears to behave similarly [15–18].

Photoreduction of the TPM dye often competes with photo-oxidation and *N*-dealkylation and either may provide the more favourable pathway by which the dye degrades. Degradation may involve either an electron or a hydrogen atom abstraction process, which are also in competition with each other [19].

The chemical structure of a dye is generally the prime factor that determines the various types of photochemical reactions a dye undergoes.

Apart from chemical structure itself, many other factors, such as the porosity of the dye support [20,21], the surrounding atmosphere, temperature, humidity and the wavelength of the incident radiation, can also influence the fading processes significantly and sometimes these factors are of overriding importance [22–30].

The dyes derived from the primary leuco dyes (primary colour formers) are not particularly light stable and are subject to fading. The search for new colour formers with better lightfastness than CVL **1** and covering all shades including black is still very active. Recently, research has concentrated on fluorans such as compounds **3**–**5** [31–33].

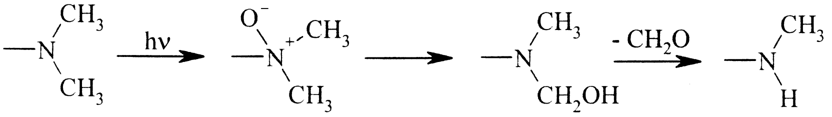


Where: R =	$-NH(CH_2)_7CH_3$	**3**
	$-N(CH_2Ph)_2$	**4**
	-*t*-Bu	**5**

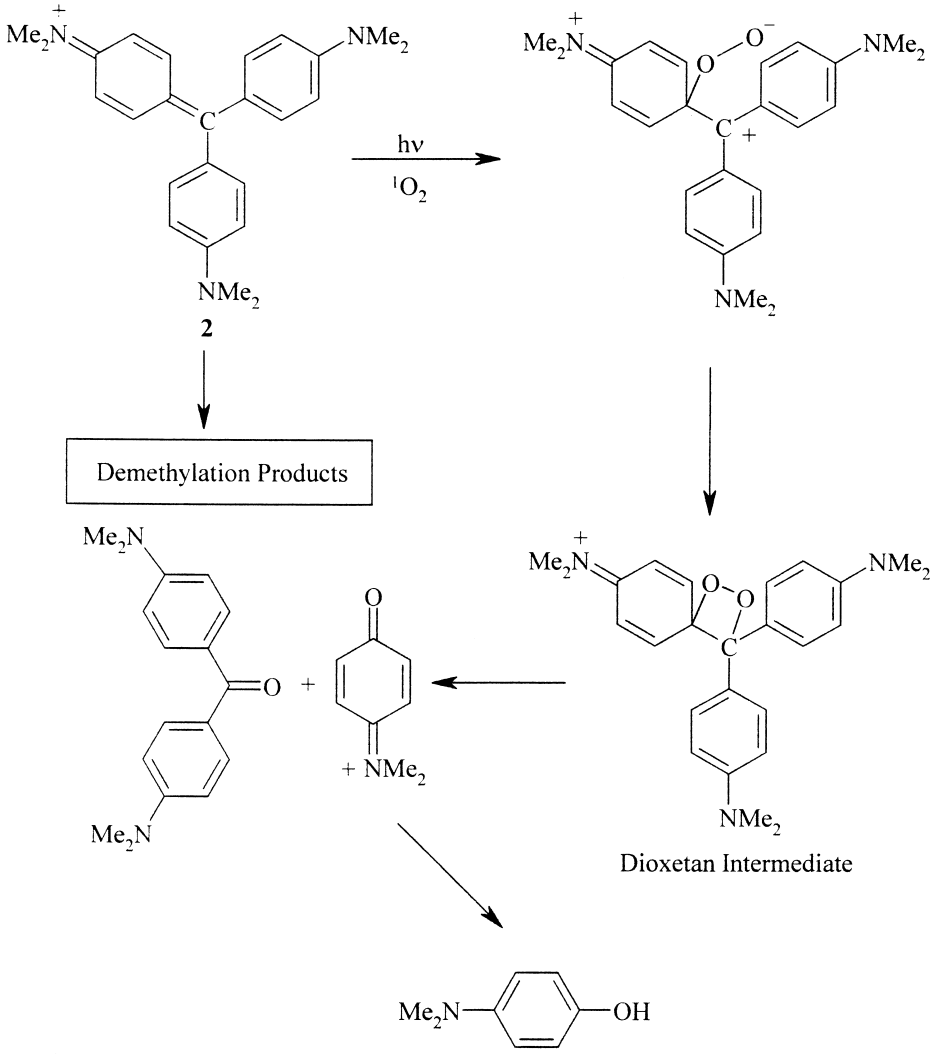
The fading of the primary dye on the clay has long been of great concern and thus knowledge of the mechanism by which the photo-decomposition of primary dyes proceeds on the clays themselves would be invaluable. We now report on the influence of singlet oxygen on the fading of some commercial TPM dyes adsorbed onto a montmorillonite clay. Accelerated fading tests were carried out and diffuse reflectance uv/visible spectroscopy used to study the progress of the fading on the clay surface.

2. Results and discussion

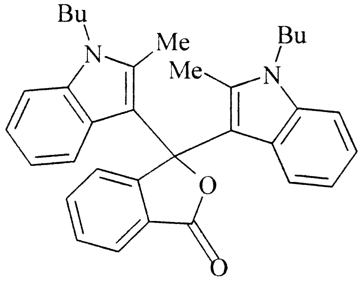
The leuco dye species examined in this study were the phthalides **1** and **6** and the fluorans **3**–**5**, which are commonly used either individually or as components for producing a black image in carbonless copying systems. The individual colours range from the almost indigo derived from **1** to the red from **6** [34] and are listed in Table 1. The acid activated clay was the commercially available Fulacolor™ produced by Laporte Absorbents from Los Trancos calcium montmorillonite mined in southern Spain.



Scheme 1.



Scheme 2. The proposed photodegradation pathways of Crystal Violet **2** [9,10].



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As there is little difference between the absorption maxima (λ_{max}) of the dyes in acidic ethanolic solution and their reflectance spectra on the clays (see Table 1), we assume that the same zwitterionic species such as **7** are formed by lactone ring opening both in solution [35] and on the clay (Scheme 3).

When dichloromethane solutions of the leuco dyes were applied to samples of the acid activated clay, Fulacolor^{TM}, the colours developed instantaneously. The dyed samples of clay were then irradiated at a fixed distance from two 30 W "artificial daylight" lamps and the rates of photofading of the primary dyes measured by monitoring both

Table 1
λ_{max} of developed primary dyes in ethanolic HCl solution and on Fulacolor™ clay

		λ_{max} (nm) Of developed dye	
	Colour	In solution	On clay
1	Blue	604	604
6	Red	538	540
3	Olive	590, 456, 436	590, 454, 430
4	Green	612, 466, 438	604, 458, 432
5	Orange	526, 494	526, 494

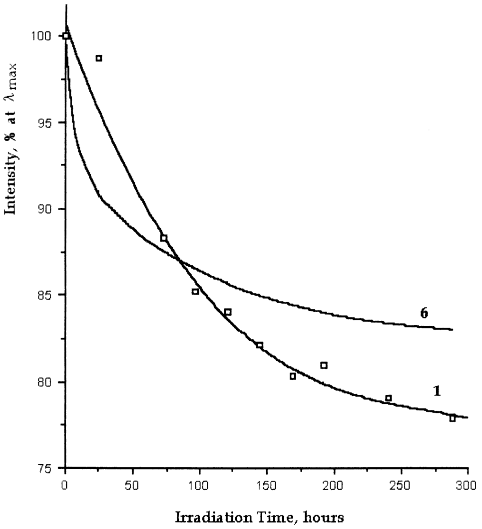


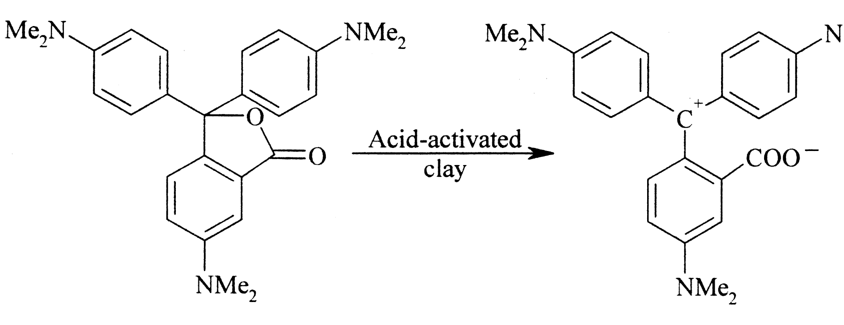
Fig. 1. Fading of phthalide dyes **1** and **6** on clay as a function of time.

changes in the λ_{max} and changes in absorbance relative to an untreated sample of Fulacolor™.

With each dyestuff, an increase in absorbance of ca. 25% was observed during the first 2 h of exposure to light. This behaviour suggests that a photo-initiated reaction occurred on irradiation, which resulted in the formation of more of the dyestuff. This was not unexpected since it is well known that the leuco forms of TPM dyes will undergo photo-reactions to their corresponding dyes [36–38]. Leuco dyes of the C–CN type split photochemically, whilst C–H types can photo-oxidise.

Fig. 1 shows the relative intensity of **1** on Fulacolor™ under irradiation as a function of time. It can be seen, that after two hours exposure to light, the increase in absorbance stopped and fading began. Continued exposure to light caused further loss of colour with a 21% decrease in the colour intensity during the course of 240 h. Concomitantly, throughout the period of exposure the sample gradually changed colour from its initial dark blue to turquoise and a bathochromic shift of 38 nm was observed in the reflectance spectrum (Fig. 2).

Attempts were made to isolate the fading products of the CVL dye cation **7**, and the other dyes, from the clay surface by successive extraction with dichloromethane, acetone and methanol, but it was extremely difficult to desorb the degradation products for analysis. Phthalic anhydride was the only product identified from the extracts by GC–MS, showing that extensive degradation of the dye had occurred. However, the developed dye **7** does resemble Crystal Violet **3** and despite lack of direct evidence, the red shift in λ_{max} and the



1 **7**

Scheme 3.

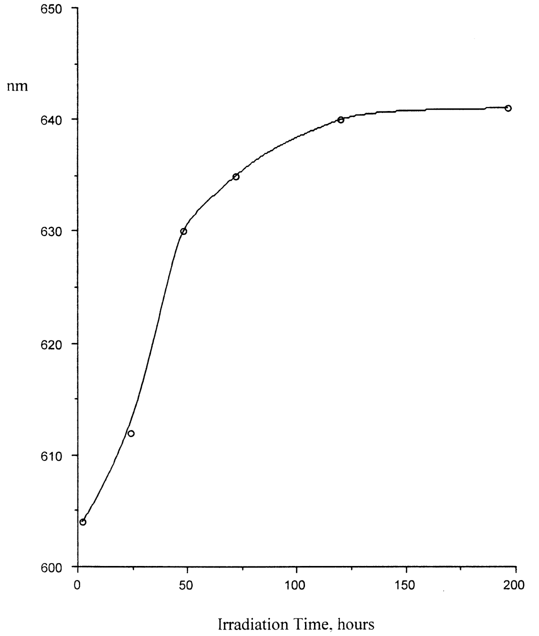


Fig. 2. Position of the λ_{max} for **1** adsorbed on Fulacolor^{TM} as a function of time of irradiation.

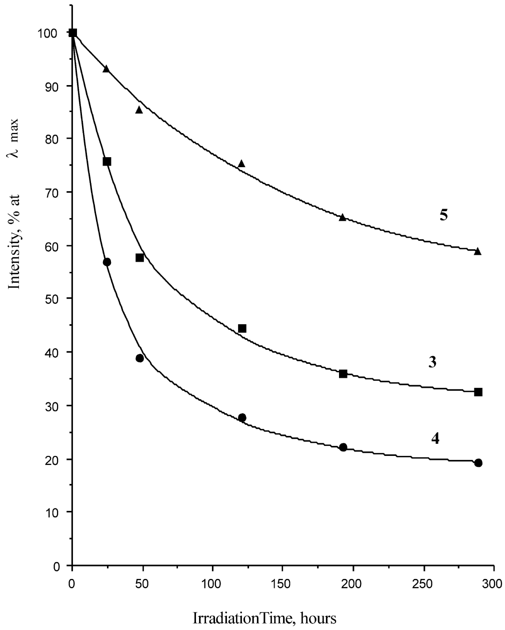


Fig. 3. Fading of fluoran dyes on Fulacolor^{TM} with respect to irradiation time at: 590 nm for **3**, 604 nm for **4** and 526 nm for **5**.

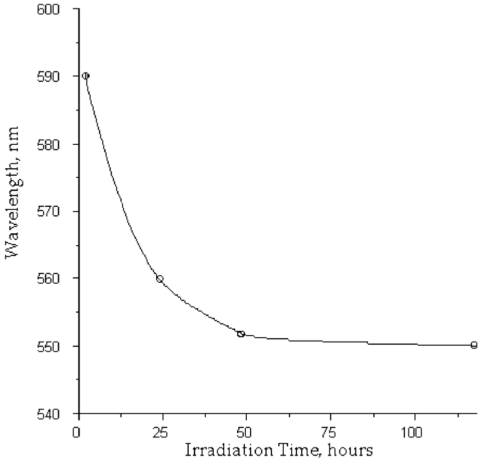


Fig. 4. Position of the λ_{max} for the dye from leuco dye from **3** adsorbed on Fulacolor^{TM} as a function of time.

change in colour from blue to turquoise suggests that a similar demethylation of a dialkylamino group is occurring with dyestuff **7**. The loss of intensity of colour also suggests that photo-oxidation to the (colourless) substituted benzophenones is taking place.

The intensity of the developed dye from **6** on Fulacolor^{TM} as a function of time with exposure to light is also shown in Fig. 1. Fading occurs and a 16% decrease of the colour intensity was observed after 240 h exposure, although there is no obvious change in the λ_{max}.

The fading of the fluoran dyes developed from **3**–**5** on exposure to light as a function of time is shown in Fig. 3. On irradiation, a sharp decrease in intensity of the dye from fluoran **3** is observed, with a 65% loss of colour over 240 h. Simultaneously, the colour rapidly changes from olive green to red. The peak at 590 nm showed a blue shift of 40 nm after only 50 h exposure to light, which accounts for the colour change (Fig. 4). The other less intense peaks at 454 and 430 nm were virtually unchanged during this period.

There is also a sharp decrease in the intensity of the green dye, derived from **4** by adsorption onto the clay, when exposed to light (Fig. 3). After 240 h exposure, 79% of the colour had been lost and the sample had turned from green to red. Unfortunately, the peak at 604 nm decreases so sharply and the spectrum becomes so complex that it is difficult to quantify the shift in λ_{max} accurately.

However, the λ_{min} at around 500 nm showed an approximately 25% increase over the same period of irradiation.

2-*t*-Butyl-6-diethylaminofluoran **5** fades on exposure to light (Fig. 3) and after 240 h of irradiation, 38% of the intensity of the dye had been lost, but without any noticeable shift in λ_{max}.

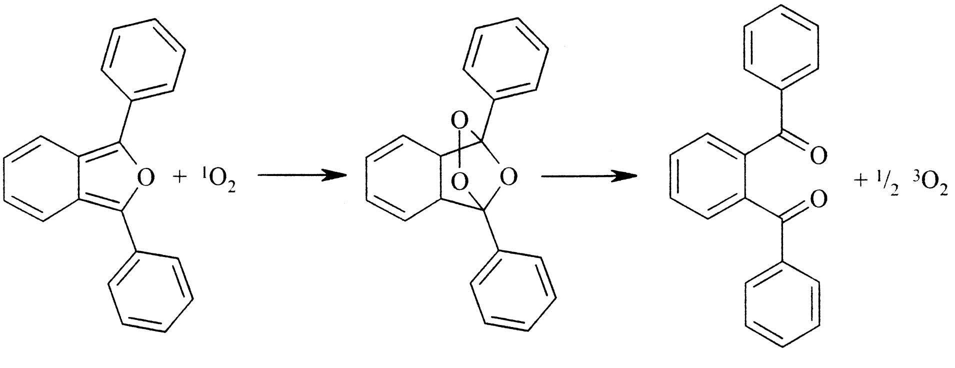
It is assumed that the fluoran dyes undergo similar reactions during exposure to light as those for the phthalides when adsorbed on to clay surfaces. A comparison of the three fluoran dyes shows that the behaviour of **5** is not quite compatible with the other two. It appears that the diamino compounds **3** and **4** are inferior to the monoamino derivative **5** as far as photo-stability is concerned. This feature may be due either to the greater chance of dealkylation of two terminal-NR_2 groups rather than one, or to the fading product(s) of the developed dye from **5** having a sufficiently similar absorption spectrum to the original dye to conceal the real situation.

To investigate the possibility of the primary dyes generating singlet oxygen, a method involving the use of 1,3-diphenylisobenzofuran (DPBF) **8** as a singlet oxygen trap was employed [39]. DPBF was chosen as the singlet oxygen acceptor because of its rapid reaction with singlet oxygen, which proceeds by formation of an endoperoxide **9** and subsequent loss of oxygen to give the diketone **10** (Scheme 4).

Measurements of the efficiency of singlet oxygen generation by the primary dyes can be directly related to the decreasing concentration of DPBF as it reacts with the reactive singlet oxygen. The leuco dyes **1** and **3–5** were adsorbed onto separate samples of the acid activated clay, Fulacolor™, which were then suspended in dichloromethane solutions of DPBF. The decrease in absorbance of the DPBF at its λ_{max} (410 nm), with respect to time, for each of the primary dyes, was then measured. In all of the fading experiments, each sample was placed at the same distance from the light source with the same cell and filter so that comparisons were valid.

Typical plots of absorbance of DPBF at 410 nm versus time are shown for CVL and fluoran **4** in Fig. 5, which provides a graphical representation of typical results obtained for the two groups of primary TPM dyes, the bridged fluoran and non-bridged phthalide dyes. Data for these and the other dyes are collected in Table 2.

It was noticed that although the irradiation was carried out using a dichromate filter, there was still a certain amount of loss of DPBF even without added dyes during the process. This is mainly due to the fact that DPBF is itself light sensitive and can be decomposed by direct photolysis. Nevertheless, it can be clearly seen that the disappearance of DPBF was accelerated considerably on adding the clay-supported dyes. After 4 h exposure to the filtered light, there was a 20% loss of DPBF itself, whilst about 80 and 90% of DPBF were consumed with added CVL and fluoran **4**, respectively. It thus appears that singlet oxygen (presumably $^1\Delta_g$) was generated by the added dyes, which then caused the decomposition of DPBF.



8 **9** **10**

Scheme 4.

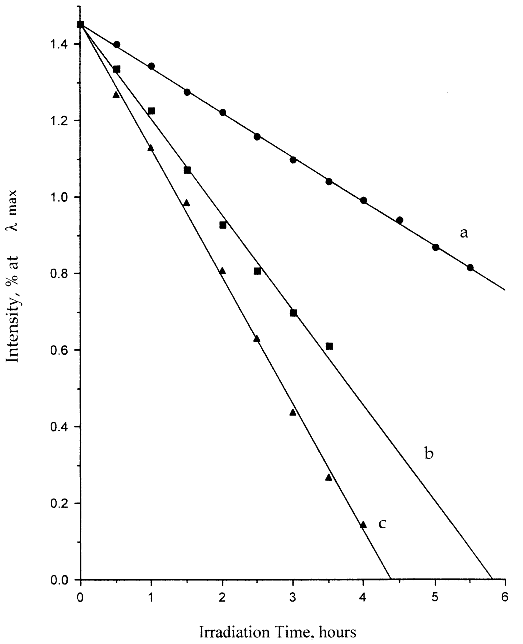


Fig. 5. Effect of dyes on DPBF consumption with respect to time; (a) DPBF only, (b) with added CVL and (c) with added fluoran **4**.

Table 2
DPBF consumption with addition of clay supported dyes

Leuco dye added	Consumption of DPBF (%) after 3 h	Fading of developed dye (%) after 240 h
6	30.6	16.5
1	38.3	21.0
5	37.6	37.9
3	42.1	65.6
4	58.6	79.3

It was also apparent from Fig. 5 that the change in concentration of DPBF with time shows a linear relationship, suggesting a zero-order reaction for the generation of singlet oxygen under the stated conditions. This is similar to the results observed by other workers for a variety of dyes [40,41].

To provide further proof that singlet oxygen was indeed involved in the reactions a known singlet oxygen quencher, diazabicyclooctane (DABCO) [9], was adsorbed onto a sample of Fulacolor™ clay and CVL added. Experiments on the destruction of DPBF in the presence this clay, showed a dramatic extension of the "lifetime" of the DPBF to over 300 h. Unfortunately, although DABCO can delay dye fading on clays it is unrealistic to use it, as the level of dye development is less than half of normal. Two possible reasons for this deleterious effect may be that the DABCO is adsorbed in preference to the CVL or the DABCO pillars between the clay layers preventing access of the leuco dye [42].

These results suggest that the coloured materials derived from the primary leuco dyes, when adsorbed on clay, act as quite efficient singlet oxygen sensitisers and apparently contribute to their own destruction. It is interesting to see that the fluorans **3**–**5** act as more efficient sensitisers than phthalides **1** and **6** (Table 2), a fact that partially explains our observations that the dyes derived from fluorans generally exhibit poorer light-fastness than those derived from phthalides.

In summary, the diffuse reflectance spectra of the dyed clays are similar to the spectra of the coloured species in acidic solutions, showing the formation of univalent cationic dyes on the clay surfaces. These coloured materials when adsorbed on the clay are subject to significant fading on exposure to light and also show changes of coloration. Whilst phthalides showed a bathochromic shift, fluorans give a hypsochromic shift and generally exhibit a higher rate of photo-decomposition than phthalides. All of the leuco dyes examined behave as quite efficient singlet oxygen sensitisers when adsorbed on the clay.

3. Experimental

All of the leuco dyes used were commercial reagents manufactured by Ciba-Geigy, Clayton, Manchester. All other reagents were purchased from Aldrich Chemical Company and used without further refinement. Fulacolor™ is a brand name of Laporte Absorbents for an acid activated, dioctahedral montmorillonite. It has an approximate specific surface area of 400 m^2 g^{-1}, measured by the B.E.T. nitrogen adsorption technique [43], and it is produced at Widnes, Cheshire.

Solution ultra violet and visible spectra were recorded in ethanol or dichloromethane on a

Hewlett Packard HP 8452A Diode Array spectrophotometer using a 1 cm path length quartz cell.

3.1. pH adjustment of the activated clays

The Fulacolor^{TM} clay (150 g) was dispersed by stirring in water so as to give a 15% by weight suspension. Sodium hydroxide (30%, w/w) was then added until the pH of the suspension reached a steady value of around 9.0. The suspension was filtered and the filter cake washed with a little water. The pH adjusted clay was then dried at 70°C for approximately 5 h, so as to give an approximate water content of 10%. The dried clay was subsequently ground mechanically in an electric grinder for 30 s and manually in a mortar with a pestle for approximately 30 min.

Representative samples were shown to have particle diameters, which were at least 50%, by weight, <2 μm by Coulter counter measurements.

3.2. Measurement of diffuse reflectance spectra

A solution (10 cm^3) of CVL **1** (0.75 g) in dichloromethane (250 cm^3) was added to a sample of pH adjusted Fulacolor clay (1 g). A 10 min adsorption/reaction time was allowed and the suspension was filtered and air-dried in the dark. The clay samples were firmly pressed into a 30 mm metal reflectance disc with a central 25×2 mm depression, which held between 0.5 and 1.0 g (depending on density) of the sample. The diffuse reflectance spectra were measured between 800 and 400 nm on a Pye Unicam SP-800B u.v./visible spectrophotometer fitted with a diffuse reflectance attachment. All spectra were compared with a Fulacolor blank. The discs were marked so that the same surface was presented to the spectrometer for subsequent measurements. A similar technique was used with the other primary dyes **3**–**6**.

3.3. Measurement of singlet oxygen production

A dichloromethane solution of DPBF **8** (3 cm^3, 5×10^{-3} M) was used to bathe the dye-treated (3×10^{-5} M) Fulacolor^{TM}, sealed in a Pyrex cell. The suspension was irradiated at room temperature at a distance of 10 cm from a pair of 49 cm long "artificial daylight" fluorescent lamps (2×30 W) through a 1 cm depth of saturated aqueous potassium dichromate filter (5×10^{-3} M, $\lambda > 500$ nm) in a Petri dish. The samples were withdrawn periodically and the bleaching of DPBF **8** was followed by monitoring the decrease in absorption at 410 nm.

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