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The inhibition of triphenylmethane primary dye fading in carbonless copying paper systems by singlet oxygen quenching bis(dithiocarbamato)nickel(II) complexes

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Abstract

Several of the dyes used in commercial carbonless copying systems act as singlet oxygen sensitisers, the production of which causes fading of the dyes [1]. A series of bis-(dithiocarbamato)nickel(II) complexes were synthesised and shown to be efficient singlet oxygen quenchers in solution in the presence of the acid activated clay. On the dry clay, however, only the hydroxyl-containing complexes were effective as they bound more efficiently to the clay. Fading was retarded more efficiently with fluoran TPM dyes, which produce more singlet oxygen, than phthalide TPM dyes. In some cases, the position and intensity of the $\lambda_{\max}$ of the dyes was preserved efficiently. © 2002 Elsevier Science Ltd. All rights reserved.

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

1. Introduction

In a previous paper [1] on the fading of carbonless copying paper primary dyes, we described the generation of singlet oxygen by triphenylmethane (TPM) dyes adsorbed on the acid activated clay, Fulacolor$^{\text{TM}}$. The dyes themselves appeared to be destroyed by the singlet oxygen and to obtain additional evidence for the intermediacy of singlet oxygen in the photofading of the primary carbonless copying paper dyes, the effects of singlet oxygen quenchers on the system were examined.

Certain metal salts and complexes, primarily those of nickel(II), and in particular dithiocarbamates, have been shown to be very efficient singlet oxygen quenchers [2–11]. Their mechanism of quenching is not known but they often have quenching rates well above 10^{10} dm^3 mol^{-1} s^{-1} [3].

2. Results and discussion

The generation of singlet oxygen was followed once again by loss of 1,3-diphenylisobenzofuran (DPBF) **1** (see Scheme 1) from a dichloromethane

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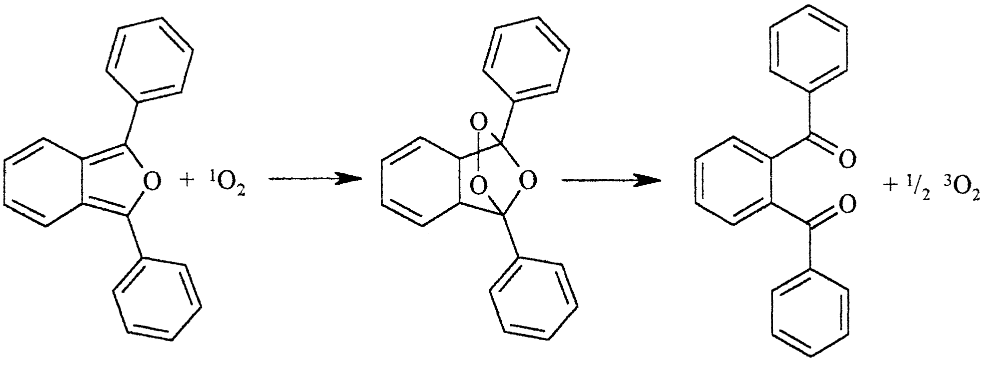

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Scheme 1. Decomposition of DPBF **1** in the presence of singlet oxygen [12].

solution on irradiation in the presence of the dyed clay [1].

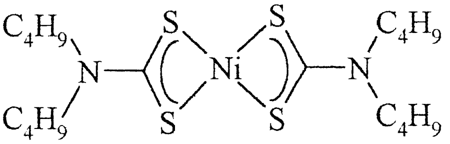
In the first instance bis(dibutyldithiocarbamato) nickel(II) **2** and bis(butyldithiocarbamato)nickel (II) **3** were synthesised and used as quenching agents, whilst the dyes which developed from crystal violet lactone (CVL) **4** and 2-dibenzyl-amino-6-diethylaminofluoran **5** on exposure to clay (see Scheme 2) were used as the sensitisers. The leuco dyes **4** and **5** were chosen first for examination as they were, respectively, the fastest fading of the phthalide and fluoran TPM dyes in our previous investigations [1].

Figs. 1 and 2 show the effects of the dibutyl complex **2** on the disappearance of DPBF in the presence of the clay adsorbed leuco dyes **4** and **5** as sensitisers. The "lifetime" of the DPBF was extended quite dramatically in both cases. After 4 h exposure, 82% of the DPBF had been consumed in the presence of the CVL, but only around 10% consumption of the DPBF occurred when the quenching agent **2** was also incorporated. In the case of sensitiser **5**, 90% of the DPBF was consumed after 4 h exposure, but less than 5% of the DPBF was consumed when **2** was added. Complete disappearance of the DPBF required over 300 h exposure, a figure which compares very favourably with less than 5 h observed in the absence of the complex **2**. Similar results were obtained with complex **3**.

Thus, the presence of the quenching reagents *in solution* extends the lifetime of the DPBF dramatically by removal of singlet oxygen. It remained to see if the inclusion of such quenchers in the formulation of the carbonless copying system would enhance the lifetime of the dyes to photofading.

Table 1
Sorption of nickel(II) complexes on Fulacolor™

Complex	Absorption at λ_{max} with addition of clay	
	Before	After
2	1.298	1.286
6	1.295	0.555
7	1.133	0.509



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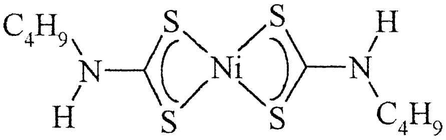

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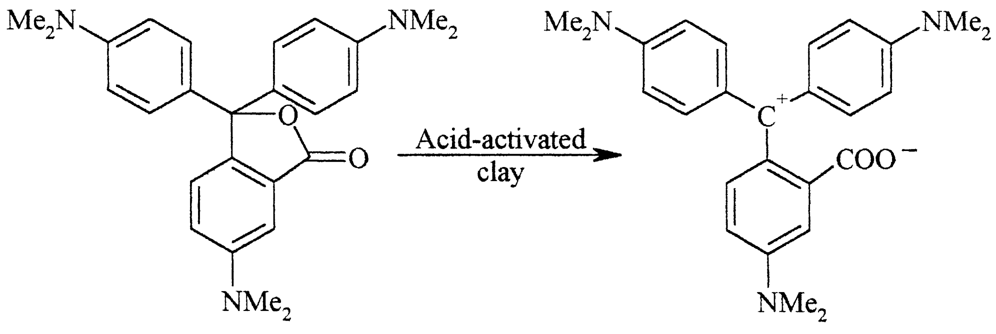

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Scheme 2. Development of the primary leuco TPM dyes on clay.

When either of the complexes **2** or **3** was included in the dry dyed-clay system, no inhibition of fading of CVL was obtained. This disappointing observation may be due either to the inability of the complexes to get near enough to the adsorbed singlet oxygen generating molecules or to the quenchers not binding strongly enough to the clay. The latter effect was confirmed by measuring the absorbance of solutions of the nickel complexes **2** and **3** in dichloromethane before and after adding clay (see Table 1). The negligible decreases in the intensity of the absorbances indicated that the complexes bind only poorly to the clay.

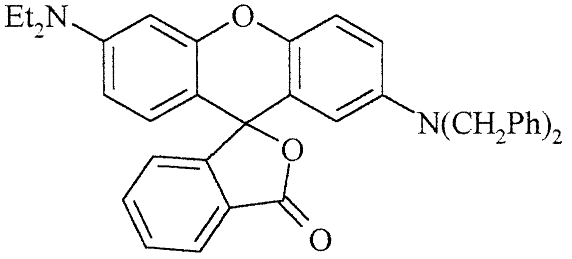
Thus, dithiocarbamatonickel(II) complexes containing polar groups, which should increase binding to the clay, were synthesised. Initially, two hydroxy derivatives, bis(2-hydroxyethyldithiocarbamato) nickel(II) **6** and bis(di-2-hydroxyethyldithiocarbamato)nickel(II) **7**, were prepared, and the effects of these complexes upon the photo-stability of the primary dyes **4** and **5** adsorbed on clay were examined. Both of these complexes **6** and **7** were found to adsorb quite strongly onto the clay (Table 1) and to inhibit DPBF decay on photolysis (Fig. 3), the complex **6** being much more effective than complex **7**.

We expected that an amino substituted dithiolato complex would bind strongly to the clay and enhance dye stability, but when derivative **8** was prepared and applied to the clay, a new effect became apparent in that less than half of the CVL offered was converted to the dye zwitterion. A similar phenomenon was observed when the purely organic quenching agent 1,4-diazobicyclo[2,2,2]octane (DABCO) **9** was added to the system [1]. This may be because these diamino compounds become protonated and either bind in preference to the CVL at the sites important to dye formation or effectively pillar the clay layers together [13] preventing dye access.

Furthermore, DABCO **9** efficiently prevented singlet oxygen generation by CVL in solution, but it was inefficient when applied to clay. In the case of the hydroxyalkyldithiocarbamatonickel(II) derivatives **6** and **7**, since the initial absorbance of the dye was shown to be about the same both in the presence and absence of the quenchers, these complexes do not appear to be blocking the active sites that develop the dyes.

Samples of dyed Fulacolor^{TM}, either in the presence or absence of the complexes **6** or **7**, were irradiated with "artificial daylight" fluorescent lamps over a period of time [1]. The inhibitory effects of each complex towards different dyes were evaluated by examining the change of colour intensity. Typical plots for one of the dyes, **5**, appears in Fig. 4 and the data for these and other leuco dyes **10**–**12** are collected in Table 2.

The phthalides **4** and **12**, which were generally more lightfast [1], showed only small or, in one case, no retardation of the rate of fading in the presence of the complexes **6** and **7** (Table 2). However, at 300 h the complex **7** had almost brought the fading of the CVL to a halt and phthalide **12** had



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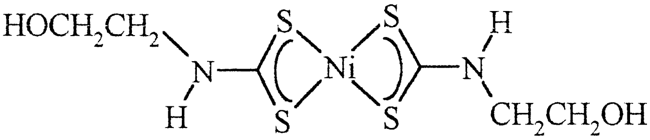

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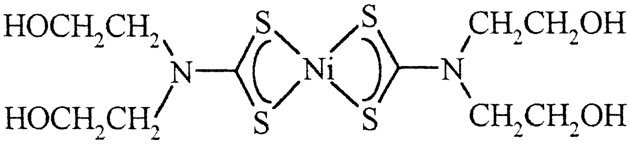

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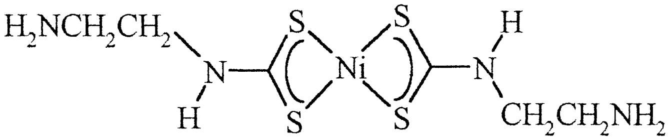
been brought to a halt. The fluorans **5**, **10** and **11**, on the other hand, showed a very large degree of retardation (*no fading at all* being observed with dye **11**) and in all cases fading had stopped before 300 h. These rates and degrees of fading are in complete accord with our previously reported observations on the ability of the dyes to produce singlet oxygen [1]. The fact that the dye **11** does not fade in the presence of the quenchers **6** and **7** whereas the others still fade slowly, suggests that reaction with singlet oxygen is the only photodegradation process for **11** whilst the others photodegrade by a combination of singlet oxygen interaction and another process; possibly N-dealkylation. This is supported by the fact that although complex **6** does not slow down the rate of fading of the CVL dye it does protect the dye from λ_{max} shift (see Fig. 5). This observation raises the possibility that singlet oxygen may also be involved in the dealkylation reactions of the dyes.

In conclusion: the effects of singlet oxygen quenchers, primarily dithiocarbamatonickel(II) complexes, on the photo-stability of primary dyes were examined both in solution and on solid clay surfaces. The simple alkyl dithiocarbamatonickel(II) complexes **2** and **3** have no obvious inhibitory affects on dye fading on clay, although these complexes showed dramatic retardation of the production of singlet oxygen in solution. Adsorption of the hydroxyalkyldithiocarbamatonickel(II) complexes **6** and **7** onto the clay resulted in improved light-fastness of the developed dyes. This was more pronounced with the fluoran dyes **5**, **11** and **12**, which we had previously shown were more efficient singlet oxygen sensitisers [1], than with the phthalide dyes **4** and **10**. The beneficial effect of the hydroxy complexes **6** and **7** appears to be a direct result of their improved ability to bind to the clay structures.

3. Experimental

All leuco dyes used were commercial reagents manufactured by Ciba-Geigy, Clayton, Man-



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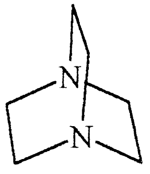

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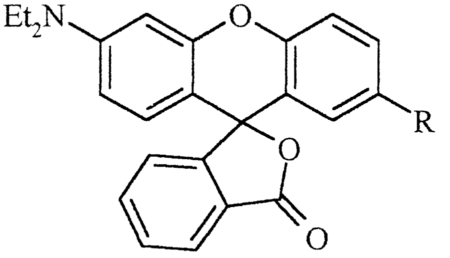
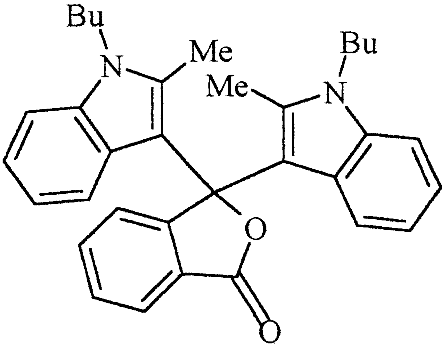


Where: R = -NH$(CH_2)_7CH_3$ **10**

-*t*-Bu **11**



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chester and were gifts from Laporte Absorbents. All other reagents were purchased freshly from Aldrich Chemical Company or BDH and used without further refinement. Fulacolor™ is a brand name of Laporte Absorbents and it is 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 [14], and it is produced at Widnes, Cheshire. Solution ultra violet and visible spectra were recorded in an appropriate solvent (ethanol or dichloromethane) on a Hewlett Packard HP 8452A Diode Array spectrophotometer using a 1 cm path length quartz cell. NMR spectra were collected on a Bruker DPX250 spectrometer.

3.1. Preparation of bis(dithiocarbamato)nickel(II) complexes

The dithiocarbamatonickel(II) complexes were prepared by an adaptation of the literature method [15,16].

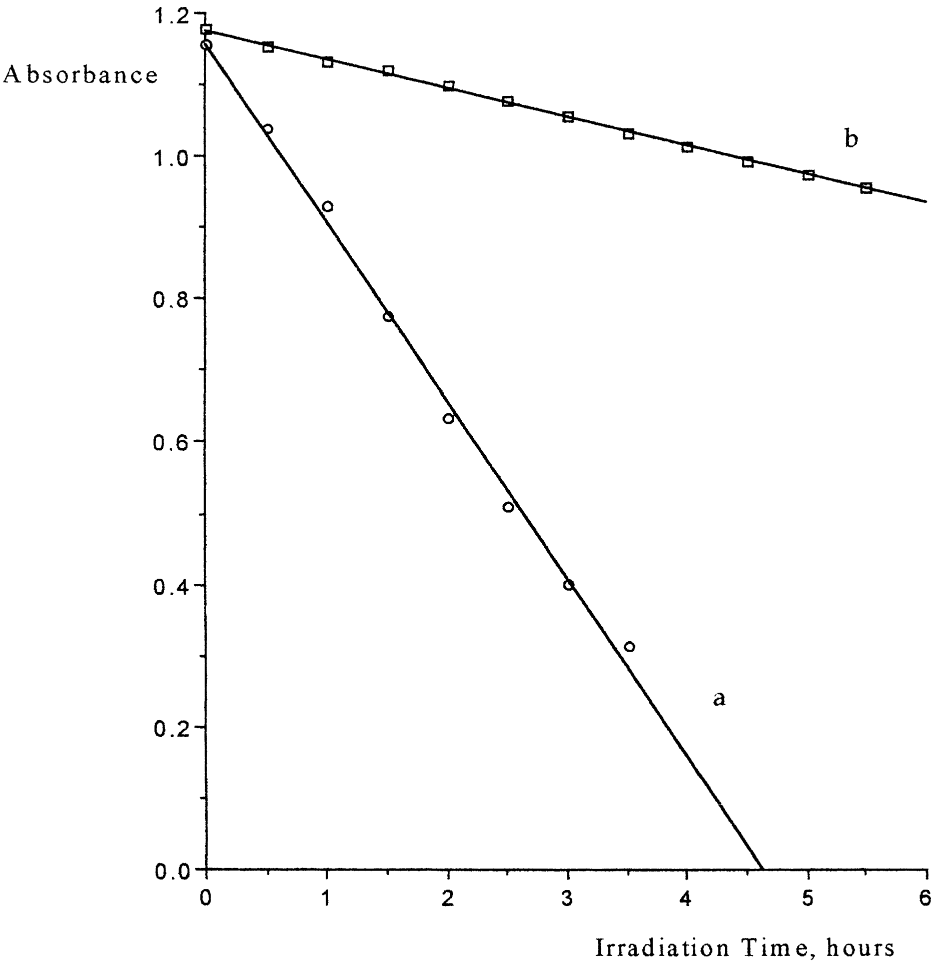

Fig. 1. Effect of quencher **2** on DPBF consumption with time in the presence of the clay supported sensitiser **4**; (a) with added **4**, (b) with added **4** and **2**.

Carbon disulphide (1.52 g, 0.02 mol) in methanol (100 cm^3) was added drop-wise over a period of half an hour to a methanolic solution (100 cm^3) of the appropriate amine (0.02 mol). When the addition was complete, an aqueous solution (200 cm^3) of hydrated nickel(II) acetate (2.49 g, 0.01 mol) was added drop-wise. The complex precipitated immediately and after filtering was recrystallised from an appropriate organic solvent (e.g. ethanol, dichloromethane, dimethylformamide depending upon the polarity of the complex) to give green crystals of the complex. The following compounds were prepared in this manner:

(a) bis(Dibutyldithiocarbamato)nickel(II) **2**, recrystallised from dichloromethane in 42% yield, m.p. 86–87 °C. δ_H (250 MHz, $CDCl_3$): 0.89–0.95 (12H, triplet, $J=7.3$ Hz, $4\times CH_3$), 1.24–1.39 (8H, sextet, $J=7.2$ Hz, $4\times CH_2$), 1.55–1.61 (8H, quintet, $J=7.2$ Hz, $4\times CH_2$), 3.48–3.54 (8H, triplet, $J=7.6$ Hz, $4\times CH_2$).

(b) bis(Butyldithiocarbamato)nickel(II) **3**, recrystallised from dichloromethane in 40% yield, m.p. 156–157 °C. δ_H (250 MHz, $CDCl_3$): 0.90–0.96 (6H, triplet, $J=7.2$ Hz, $2\times CH_3$), 1.32–1.40 (4H, sextet, $J=7.2$ Hz, $2\times CH_2$), 1.55–1.61 (4H, quintet, $2\times CH_2$), 3.38–3.46 (4H, sextet, $J=6.4$ Hz, $2\times CH_2$), 6.55–7.00 (2H, broad, $2\times NH$).

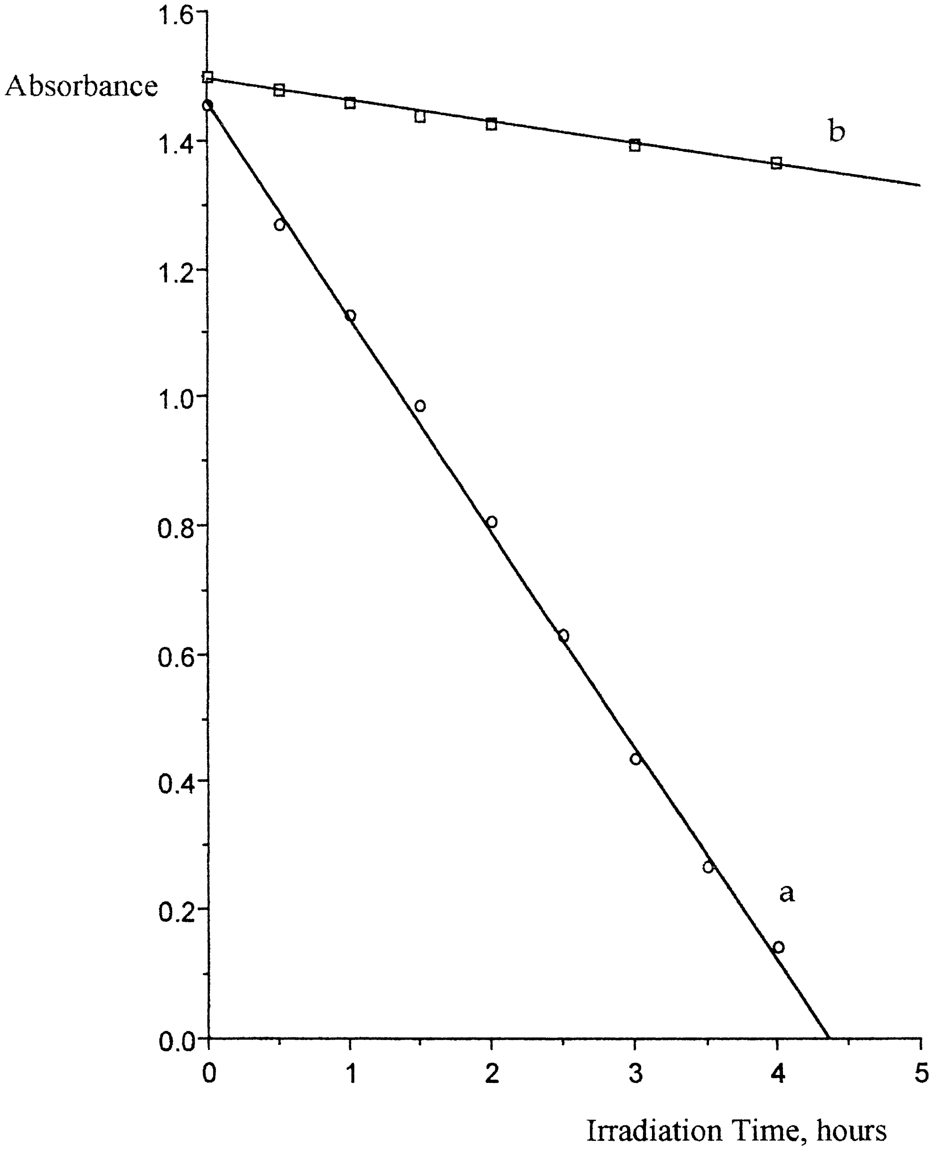

Fig. 2. Effect of quencher **2** on DPBF consumption with time in the presence of the clay supported sensitiser **5**; (a) with added **5**, (b) with added **5** and **2**.

(c) bis(2-Hydroxyethyldithiocarbamato)nickel(II) **6**, recrystallised from ethanol in 93% yield, m.p. 150 °C. δ_H (250 MHz, DMSO-d_6): 3.28–3.32 (4H, triplet, J = 5.6 Hz, 2×CH_2), 3.45–3.55 (4H, sextet, J = 5.2 Hz, 2×CH_2), 4.88–4.92 (2H, triplet, J = 5.2 Hz, 2×OH), 10.3–10.7 (2H, broad, 2xNH).

(d) bis(Di-2-hydroxyethyldithiocarbamato)nickel (II) **7**, recrystallised from ethanol in 43% yield, m.p. 212 °C. δ_H (250 MHz, DMSO-d_6): 3.60–3.63 (8H, triplet, J = 5.1 Hz, 4×CH_2), 3.66–3.68 (8H, multi, J = 4.8 Hz, 4×CH_2), 4.99–5.03 (4H, triplet, J = 5.2 Hz, 4×OH).

To obtain bis(2-aminoethyldithiocarbamato)-nickel(II) **8**, ethylenediamine was used in the reaction with CS_2 (two ligands are formed, the zwitterionic salt and a small amount of the bis-dithiocarbamate [17]). By adding excess diamine (amine/carbon disulphide 1:4 mole ratio) the

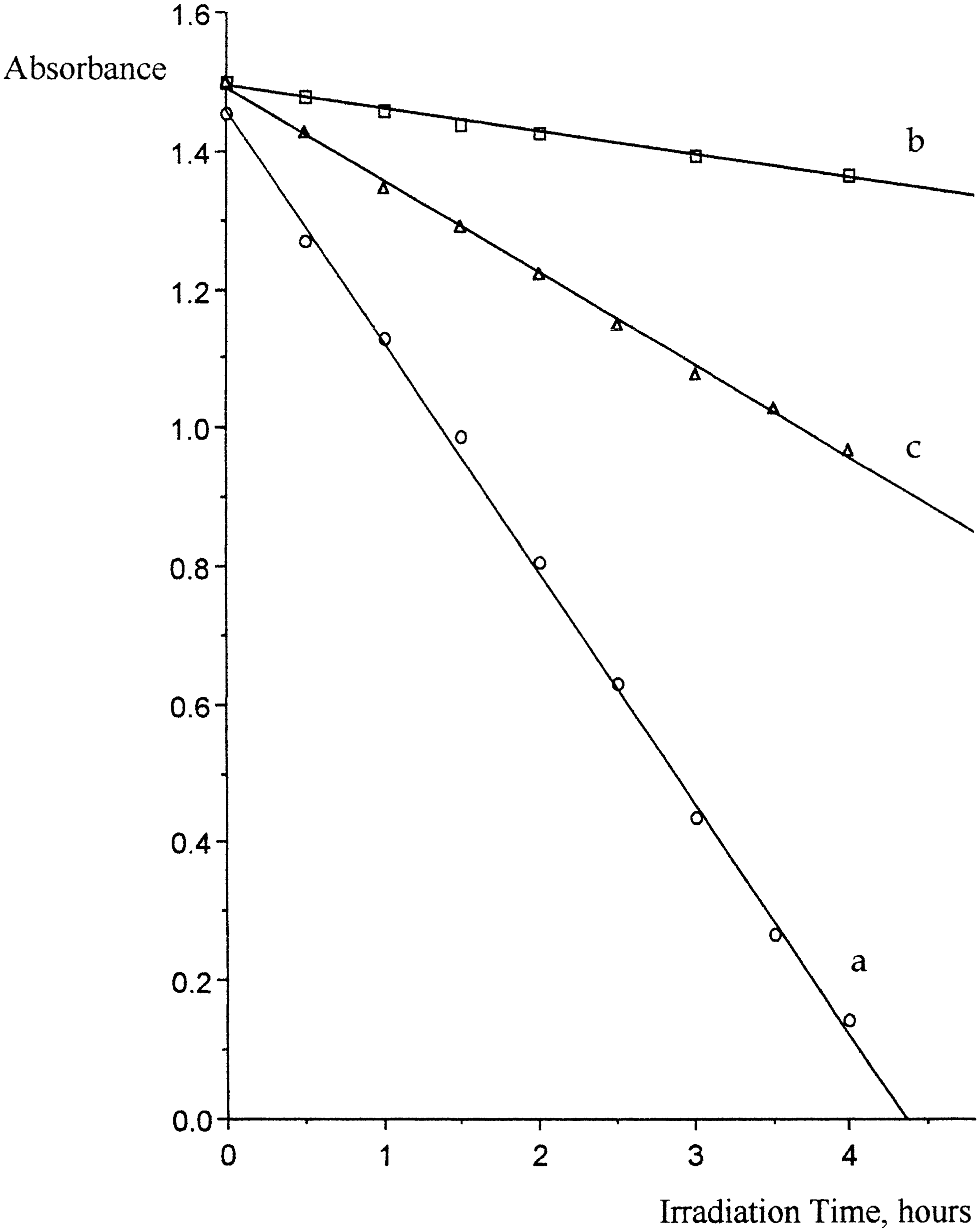

Fig. 3. Effectiveness of nickel complexes **6** and **7** for quenching singlet oxygen generated by CVL **4** on clay and measured by DPBF decay; (a) with added **4**, (b) with added **4** and **6**, (c) with added **4** and **7**.

zwitterionic salt was precipitated as a white or pale yellow solid. After filtering, dilute sodium hydroxide was used to dissolve the salt before adding aqueous nickel(II) acetate solution, yield 23%, m.p. 168 °C. The complex **8** was not fully characterised due to solubility problems.

3.2. pH adjustment of the activated clays

The Fulacolor^{TM} clay (150 g) was dispersed with 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

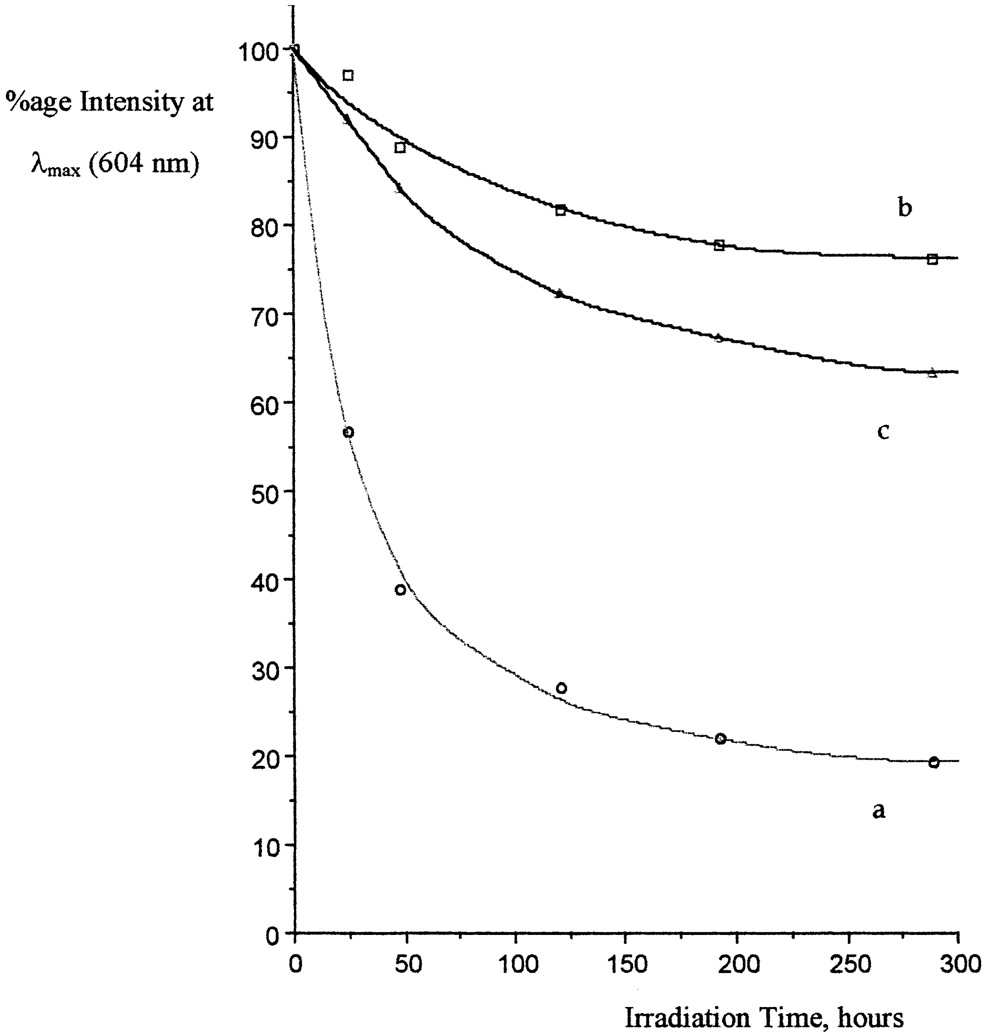

Fig. 4. Effect of dithiocarbamatonickel(II) complexes **6** and **7** on the photo-stability of the green dye derived from **5** on Fulacolor™; (a) on untreated Fulacolor™, (b) on Fulacolor™ treated with **6**, (c) on Fulacolor™ treated with **7**.

Table 2
Effects of quenchers **6** and **7** on the fading of dyes

Leuco dye	% Fading of dye in 300 h		
	Without complexes	With complex **6**	With complex **7**
4	22	22	15
12	17	12	13[a]
5	80[a]	24[a]	36[a]
10	67	22[a]	1[a]
11	41	0[a]	0[a]

[a] Essentially, the dyes were no longer fading at this time.

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 clays were subsequently ground mechanically in an electric grinder for 30 s and manually in a mortar with 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.

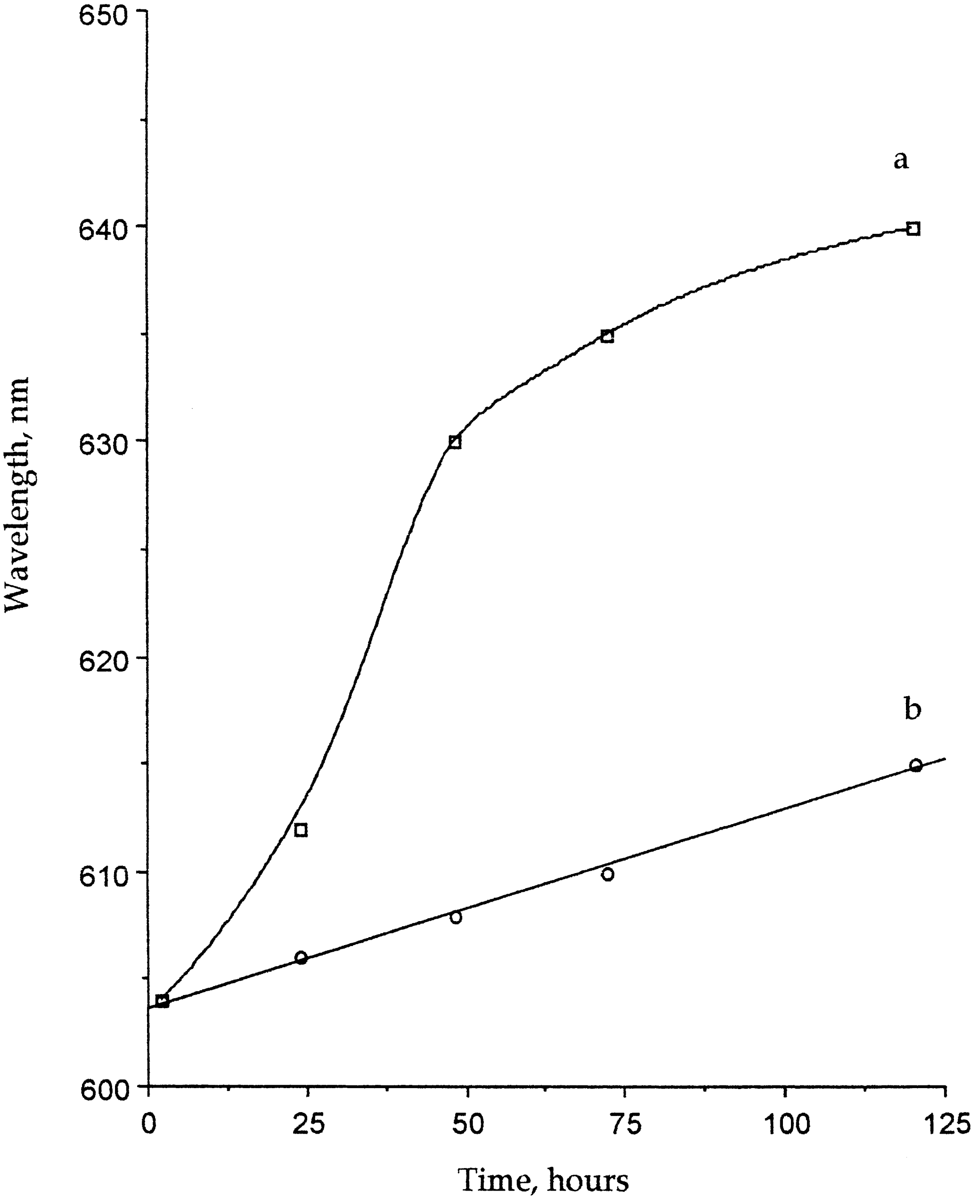

Fig. 5. Position of the λ_{max} for developed CVL on Fulacolor™ as a function of time; (a) on untreated Fulacolor™ and with complex **7**, (b) on Fulacolor™ treated with complex **6**.

*3.3. Measurement of the adsorption of the nickel(II) complexes **2**, **6** and **7** onto Fulacolor™*

Solutions (2.0×10^{-4} M) of each complex (5×10^{-5} mol) in tetrahydrofuran (250 cm^3) were prepared. Fulacolor™ clay (0.5 g) was added to aliquots (25 cm^3) of the tetrahydrofuran solution and adsorption allowed to occur for 20 min at room temperature. The suspensions were filtered and the absorption spectra of the solutions were then measured between 800 and 350 nm and compared with the absorbance before addition of the clay. The relative percentage adsorption of each complex was determined at the absorption maximum (all ca. 385 nm) of the corresponding complex.

3.4. Measurement of diffuse reflectance spectra

Dichloromethane solution (10 cm^3) of CVL **4** (0.75 g, 1.8 mmol/250 cm^3) was added to a sample of pH adjusted Fulacolor^{TM} clay (1 g), with or without pre-treatment by the complexes as above. A 10 min adsorption/reaction time was given and the suspension filtered and air-dried in the dark. The clay was pressed firmly into a metal reflectance disc and the diffuse reflectance spectra were measured between 800 and 400 nm on a Pye Unicam SP-800B UV/visible spectrophotometer fitted with a diffuse reflectance attachment. The metal sample discs were 30 mm in diameter with a central 25×2 mm depression, which held between 0.5 and 1.0 g (depending on density) of sample. All spectra were compared with a Fulacolor^{TM} blank. The discs were marked so that the same surface was presented to the spectrometer on subsequent measurements.

Similar measurements were made with the other primary dyes **4**–**7**.

3.5. Measurement of singlet oxygen production

A dichloromethane solution of DPBF **1** (3 cm^3, 5×10^{-3} M) and the nickel(II) complex (**2**, **3**, **6** or **7**) (3×10^{-5} M) was used to bathe the dye-treated Fulacolor^{TM} (4 mg), sealed in a Pyrex cell. The suspension was irradiated at a distance of 10 cm at room temperature with a pair of 49 cm long "artificial daylight" fluorescent lamps (2×30 W) through a 1 cm depth of 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 **9** was followed by monitoring the decrease in absorption at 410 nm.

Acknowledgements

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