PHOTOCHEMICAL FADING AND PHOTOSTABILIZATION OF THE CRYSTAL VIOLET LACTONE COLOUR FORMER SYSTEM

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Summary

The photochemistry and photofading of the leuco and dye forms of the crystal violet lactone colour former system have been examined under various conditions using UV absorption, flash photolysis and high performance liquid chromatography techniques as well as hydroperoxide analysis. Colour production in solution is very much dependent on the acid concentration attaining a maximum at 90 vol.% acetic acid in acetonitrile. The leuco–dye equilibrium is an important factor in controlling the light stability of the system; photofading is shown to be essentially a photo-oxidative free-radical process followed by oxygen attack generating peroxides. The latter are effectively destroyed by a well-known hydroperoxide decomposer, nickel dialkyldithiocarbamate, which thus imparts stability to both the leuco and the dye forms of the colour former. Mechanisms are proposed to account for the results and the commercial implications of the light stability data to the practical use of colour formers are discussed.

1. Introduction

Colour formers are colourless precursors to dyestuff molecules which are readily rendered coloured by the action of a co-reactant. This process forms the basis of what is generally known as the carbonless copy system. In this a leuco dyestuff (or appropriate mixture of leuco dyes) is dissolved in a suitable organic solvent and the solution microencapsulated in gelatin or some synthetic material. The microcapsules are coated onto the back of a sheet of paper. A second sheet of paper has its upper surface coated with a co-reactant (usually a Brönsted or Lewis acid) capable of converting the colour former into a coloured dye. When the two sheets of paper are put together and suitable "print" pressure is applied a coloured image is produced.

One of the most widely used colour formers for this purpose is crystal violet lactone which on treatment with a suitable co-reactant gives a typical brilliant cobalt-blue colour by the reaction

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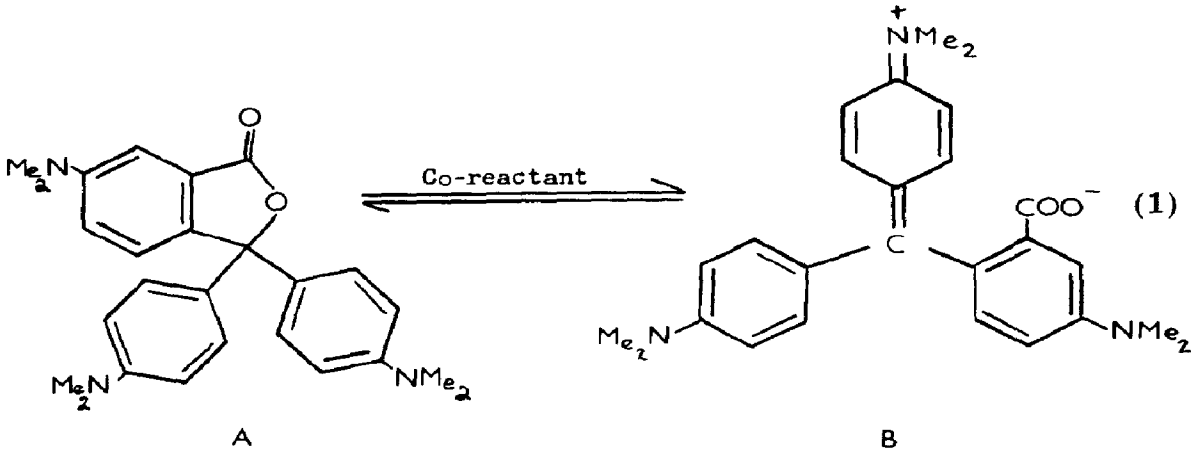


In reaction (1), B is the coloured form, the positive charge on the nitrogen being extensively delocalized throughout the ring system. Modern co-reactants are normally acid activated clays, phenol formaldehyde resins, metal, *e.g.* zinc, chelated resins or metal salts such as zinc salicylate.

One major problem associated with the use of these systems, however, is the poor light stability of the "dye". The product B in reaction (1) is related to the well-known triarylmethane dye, crystal violet. This class of dyestuff is known to be sensitive to the effect of light exposure, particularly in the presence of oxygen and when present in reductive–polar environments. Much of the research on the photochemistry and fading on this class of dye has centred on its properties in textile fibres such as cotton and Orlon. The mechanisms involved are complex and little understood but recent work has established that the following general scheme may be important [1 - 5]:

$$D^+ \longrightarrow {}^1D^+ \longrightarrow {}^3D^+ \qquad (D^+ \equiv \text{dye})$$

$${}^3D^+ + \text{solvent} \longrightarrow D^{\cdot +} + e^-(\text{solvated})$$

$$D^+ + e^-(\text{solvated}) \longrightarrow D^{\cdot} + \text{solvent}$$

$$e^-(\text{solvated}) + O_2 \longrightarrow O_2^{\cdot -} + \text{solvent}$$

$$O_2^{\cdot -} + H_2O \rightleftharpoons HO_2^{\cdot} + OH^-$$

$$2HO_2^{\cdot} \longrightarrow H_2O_2 + O_2$$

$$D^+ + H_2O_2 \longrightarrow \text{oxidized products}$$

Scheme 1.

In this scheme the triplet state of the dye cation reacts with the solvent to give a solvated electron that can undergo further reactions with the dye to give hydrogen peroxide and the dye radical. Hydrogen peroxide is known to react with basic triarylmethane dyes on photolysis to give ketone products [3, 5].

Several workers have examined ways of improving the photostability of these dyes and at the same time gained some further understanding of the fading mechanisms. Allen *et al.* [6] found that electron traps inhibited photofading of triarylmethane dyes in poly(vinyl alcohol) film, confirming Scheme 1 above, while other workers [7] have found that certain nickel complexes, such as nickel dibutyldithiocarbamate, will inhibit the photo-oxidation of these dyes on silica gel and suggested that a singlet-oxygen mechanism was involved in dye fading. However, it is well known that nickel complexes of this type destroy hydroperoxides in a dark reaction [8] and such a mechanism would add support to Scheme 1 above implicating the oxidative role of hydrogen peroxide.

In this work we have examined the photochemistry of the equilibrium in reaction (1) for crystal violet lactone both in solution and in print with particular emphasis on photostability as measured by absorption and reflectance spectroscopy and high performance liquid chromatography (HPLC). Free-radical formation during light exposure is measured by conventional microsecond flash photolysis, confirming the involvement of the dye radical in Scheme 1, and methods of inhibiting dye fading are investigated. Our results show that the equilibrium in reaction (1) is important in controlling dye photofading and that peroxide decomposers, such as nickel dibutyldithiocarbamate, are effective stabilizers in both solution and print.

2. Experimental details

2.1. Materials

The crystal violet lactone was supplied by ICI Organics Division PLC, Manchester. The compound was recrystallized from butan-1-ol (with carbon screening), then twice from toluene. The resulting material was found to be chromatographically pure by both thin-layer chromatography and HPLC. The solvents toluene, chloroform, 2-propanol, ethanol, acetonitrile and glacial acetic acid were all of "AnalaR" quality and obtained from Fisons (U.K.) Ltd. Crystal violet dye was obtained from Hopkins & Williams Ltd., U.K.

2.2. Spectroscopic measurements

Absorption spectra were recorded using a Pye SP8-100 digital scanning spectrophotometer while reflectance spectra on actual prints were recorded using a Perkin–Elmer Lambda 9 scanning spectrophotometer coupled to a microcomputer.

2.3. Flash photolysis

Transient absorption spectra were recorded using a conventional microsecond kinetic apparatus coupled to a Tetronix DM6 storage oscilloscope. Flash excitation was obtained in two xenon-filled quartz tubes triggered at 10 kV (about 30 J) and the spectrum was obtained via a 150 W tungsten–halogen monitoring source.

2.4. Light exposures

Samples were exposed in a Microscal unit (Microscal Ltd., London) utilizing a 500 W high pressure mercury tungsten lamp (50 °C; relative humidity, ambient) and a Hanovia photochemical reactor using a 100 W medium pressure mercury vapour lamp. Samples were also exposed in a Xenotest-150 weatherometer (Original Hanau, G.m.b.H., F.R.G.) utilizing 1500 W high pressure xenon arc lamps (45 °C; relative humidity, 50%).

2.5. Preparation of printed plates

A standard solution of 1 g l^{-1} crystal violet lactone was prepared in a mixture of 70wt.%Meflex–30wt.%toluene. Meflex (a registered trademark of Imperial Chemical Industries PLC) is a commercially available solvent used extensively in acid clay colour former systems. The solution was then applied to printing paper using an R.K. Precision Gravure Proof Printer. A list of stabilizers examined at 1 wt.% is given in Table 1, including the commercial and chemical names and suppliers.

2.6. Chromatographic analysis

Solutions of crystal violet lactone (1 g l^{-1}) in toluene with various amounts of nickel dibutyldithiocarbamate were exposed in a Xenotest-150 irradiation machine and subsequently analysed by HPLC (Hewlett–Packard 1084-B model) utilizing a Hypersil-capped ODS column at 40 °C (flow rate,

TABLE 1

List of stabilizer compounds studied

Commercial name	*Chemical*	*Suppliers*
—	4-Hydroxy-2,2,6,6-tetramethyl-piperidinyl-*N*-oxy	Aldrich Chem. Co. Ltd., U.S.A.
—	Tetracyanoethylene	Aldrich Chem. Co. Ltd., U.S.A.
DABCO	1,4-diazabicyclo[2.2.2]octane	Aldrich Chem. Co. Ltd., U.S.A.
NDBDC	Nickel dibutyldithiocarbamate	E. I. du Pont de Nemours & Co. Ltd., U.S.A.
Goodrite 3114	1,3,5-Tris(3,5-di-*tert*-butyl-4-hydroxylbenzyl) isocyanate	B. F. Goodrich & Co. Ltd., U.S.A.
Tinovin 770	Bis(2,2,6,6-tetramethyl-4-piperidinyl) sebacate	Ciba–Geigy Corp., Switzerland
Topanol OL	2,6-Di-*tert*-butyl-4-methyl-phenol	ICI Ltd., U.K.
Weston 618	Distearylpentaerythrityl diphosphite	Borg–Warner Corp., Holland
Cyasorb UV531	2-Hydroxy-4-*n*-octoxybenzo-phenone	American Cyanamid Co., U.S.A.

2 cm^3 min^{-1}) and a UV detector set at 270 nm. The percentage colour former (leuco) remaining was measured using the expression

$$\text{Percentage remaining} = \frac{100T_1}{C_1}\frac{C_2}{T_2}$$

where T_1 is the integration value for the toluene peak prior to photolysis, T_2 is the integration value for the toluene peak in the mixture being analysed, C_1 is the integration value for the colour former peak prior to photolysis and C_2 is the integration value for the colour former peak in the mixture being analysed.

2.7. *Preparation of crystal violet lactone free radical*

Crystal violet lactone (0.3 g) was dissolved in glacial acetic acid (5 cm^3) and the solution was degassed with nitrogen for 10 min. Titanous chloride (2 cm^3 of 1 M solution) was then added to give a bright-yellow-coloured solution of the free radical formed by [9]

$$(Ph_3)C^+ + Ti^{3+} \longrightarrow Ph_3C^\cdot + Ti^{4+} \quad (2)$$

Part of the solution was then rapidly charged to a quartz cell (1 cm^3) for the recording of its absorption spectrum.

2.8. *Hydroperoxide analysis*

Irradiated solutions of crystal violet lactone (10^{-4} M) in 67vol.%(acetic acid)–33vol.%chloroform were degassed with nitrogen for 2 min. To aliquots (25 cm^3) of the solution was added 50% aqueous potassium iodide (1.0 cm^3) followed by further nitrogen purging for 2 min. The solutions, after standing in the dark for 30 min, were analysed at 470 nm. The absorbance was calibrated directly against hydrogen peroxide concentration [1] as parts per million of active oxygen using the method of Banerjee and Budka [10].

3. Results and discussion

The absorption spectra of crystal violet lactone in acetonitrile and its corresponding "dye" in glacial acetic acid–acetonitrile solution are compared in Fig. 1. The leuco form has an absorption maximum at 270 nm while the coloured form absorbs strongly at 605 nm. Mixtures of acetic acid with acetonitrile were found to give the most intense colouration, for a 10^{-4} M solution, at a ratio of 90:10 by volume. The extinction coefficient ϵ (l mol^{-1} cm^{-1}) was recorded for each solution and the results plotted in Fig. 2. It is seen that a maximum extinction coefficient of only 28 000 is observed over the entire solvent ratio range. At acid concentrations higher than 90 vol.% the extinction coefficient decreased dramatically, probably owing to protonation of the dimethylamino groups on the molecule. The extinction coefficient of pure crystal violet dye was similarly recorded under the same conditions and found to be much higher, 109 000 at 586 nm. This indicates

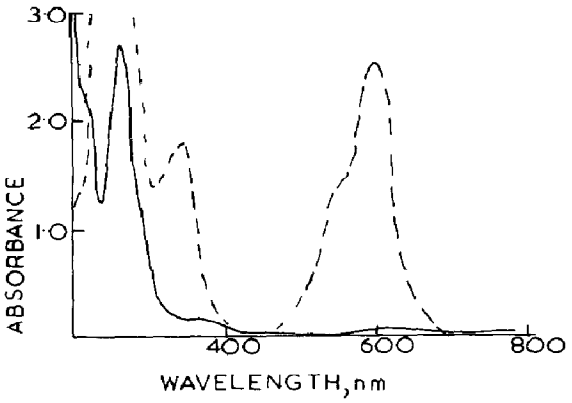


Fig. 1. Absorption spectra of crystal violet lactone in acetonitrile (——) and 90vol.%-(acetic acid)–10vol.%acetonitrile (– – –).

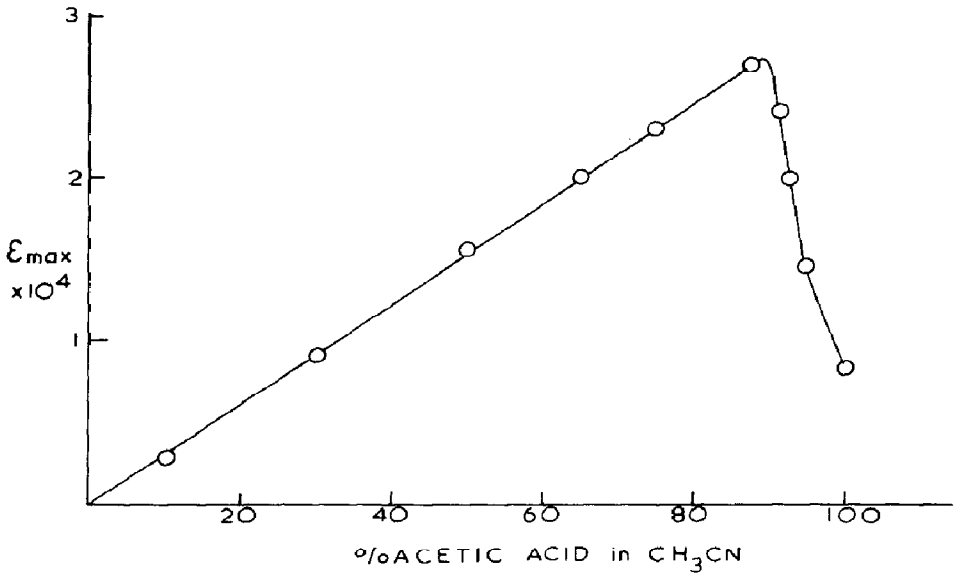


Fig. 2. Plot of ϵ_{max} (l mol^{-1} cm^{-1}) for crystal violet lactone (10^{-4} M) colour *vs.* volume percentage acetic acid in acetonitrile solvent.

that even under these strongly acidic conditions the major portion of crystal violet lactone is in the leuco form.

The importance of the equilibrium in the photostability of the crystal violet lactone colour is demonstrated by the results in Figs. 3 and 4. The former shows the effect of acetic acid concentration on the extinction coefficient of the dye during irradiation in a Microscal unit while the latter compares this data in terms of a percentage colour loss. From the results it is seen that fading increases with increasing acid concentration up to 80 vol.% and this is evidently associated with greater initial colour production (Fig. 2). At higher concentrations of acid (95 vol.%) the fading rate is slower owing to less colour production and a balancing effect on the equilibrium at such high acid concentrations, *i.e.* as fast as the colour is being consumed more is being

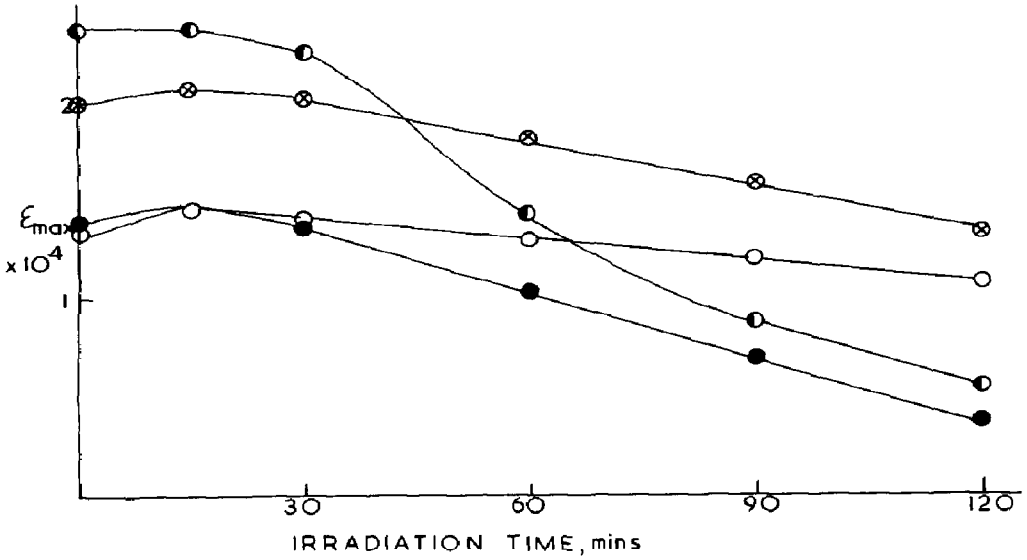


Fig. 3. ϵ_{max} (l mol^{-1} cm^{-1}) *vs.* irradiation time in minutes in a Microscal unit of crystal violet lactone colour in 30 vol.% (○), 65 vol.% (⊗), 80 vol.% (◐) or 95 vol.% (●) acetic acid in acetonitrile (crystal violet lactone, 10^{-4} M).

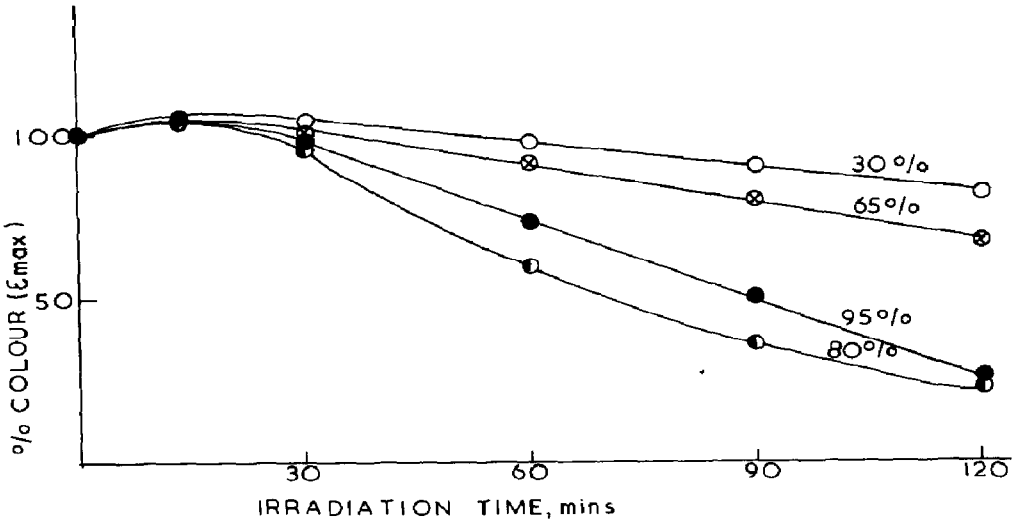


Fig. 4. Percentage retention of colour *vs.* irradiation time in a Microscal unit of crystal violet lactone (10^{-4} M) in 30 vol.% (○), 65 vol.% (⊗), 80 vol.% (◐) or 95 vol.% (●) acetic acid in acetonitrile.

produced. This latter effect is noticeable initially from Fig. 4 when the ϵ_{max} increases during the early stages of irradiation. Similar results were obtained in the Xenotest-150 irradiation unit. The effect of oxygen on dye fading is shown by the results in Fig. 5. These results show that oxygen accelerates dye fading, which confirms the findings of Kuramoto *et al.* [7]. These workers concluded that singlet oxygen was involved in dye fading, but the results in Fig. 6 and below shows that this is clearly not the case. In Fig. 6 it

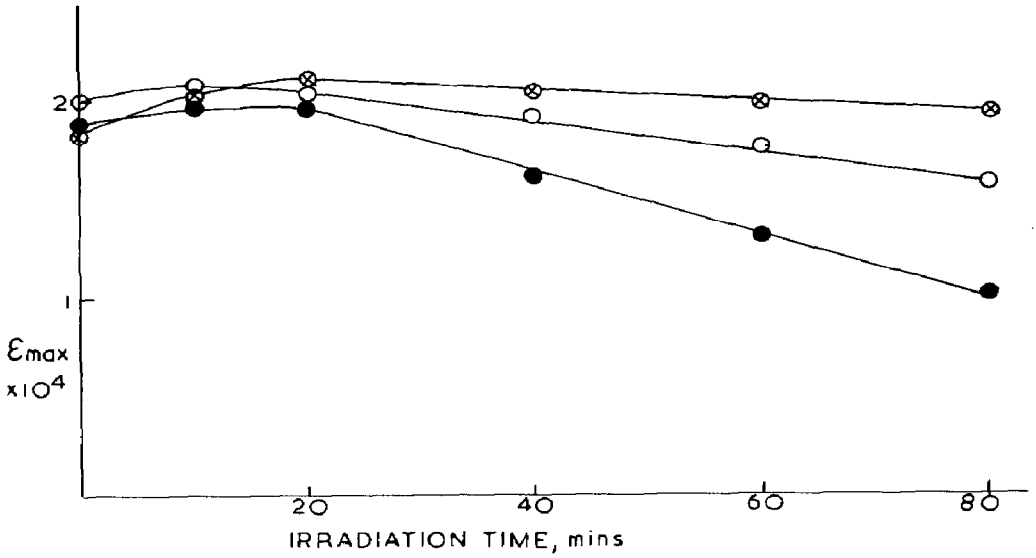


Fig. 5. ϵ_{max} (l mol^{-1} cm^{-1}) *vs.* irradiation time in minutes in a Microscal unit of crystal violet lactone (10^{-4} M) in 65 vol.% acetic acid in acetonitrile in the presence of air (○), O_2 (●) or N_2 (⊗).

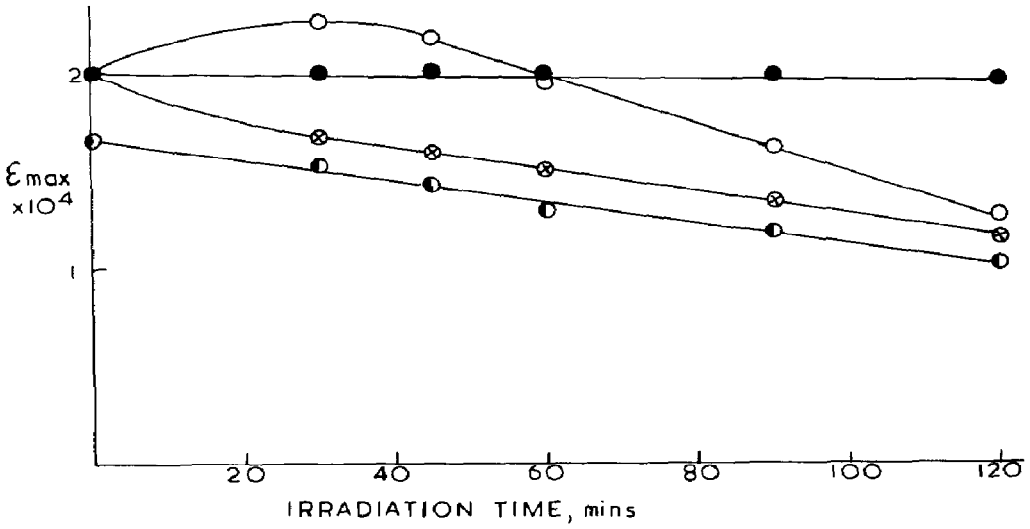
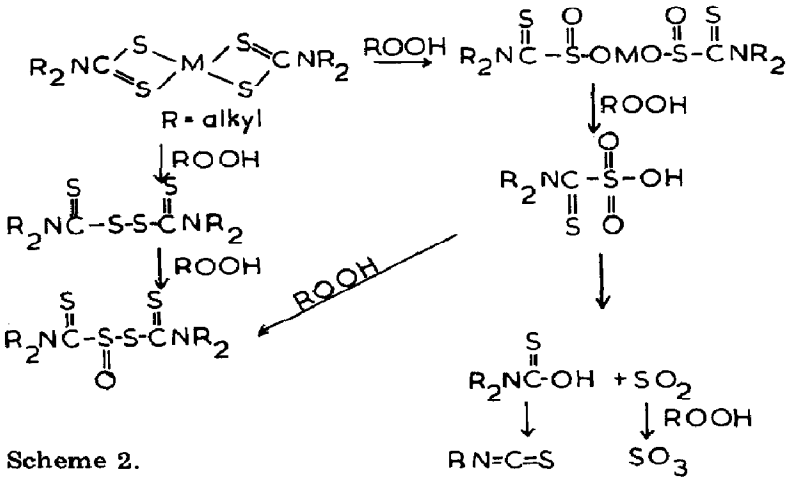


Fig. 6. ϵ_{max} (l mol^{-1} cm^{-1}) *vs.* irradiation time in a Microscal unit of crystal violet lactone (10^{-4} M) in 65 vol.% acetic acid in acetonitrile in the presence of no additive (○), nickel dibutyldithiocarbamate (●), tetracyanoethylene (⊗) or DABCO (◐) (10^{-4} M each).

is seen that, while addition of either tetracyanoethylene, an electron trap, or DABCO, a singlet-oxygen scavenger, has little effect on the photofading of the crystal violet lactone colour, the presence of nickel dibutyldithiocarbamate has a marked stabilizing effect. The latter is a well-known peroxide decomposer in commercial thermoplastics [8] and therefore confirms the involvement of hydrogen peroxide or other peroxidic species in dye fading as was indicated in Scheme 1 above.

Metal dialkyldithiocarbamates undergo a dark reaction with hydroperoxides as shown in Scheme 2 and the main transformation products, namely organosulphites and sulphur oxides, will react further with any hydroperoxides or hydrogen peroxide to give inactive products [8].



Scheme 2.

The stabilizer work was extended to cover the wide range of additives shown in Table 1; print fading was examined after an initial 100 min of irradiation using reflectance spectroscopy. All the additives shown in Table 1 other than nickel dibutyldithiocarbamate were completely ineffective in protecting the dye, confirming our findings from solution photolysis. In contrast, all the other additives accelerated the fading of the colour and an example of this effect compared with that of the nickel complex is shown in Fig. 7. Apart from protecting the colour the nickel complex also protects the

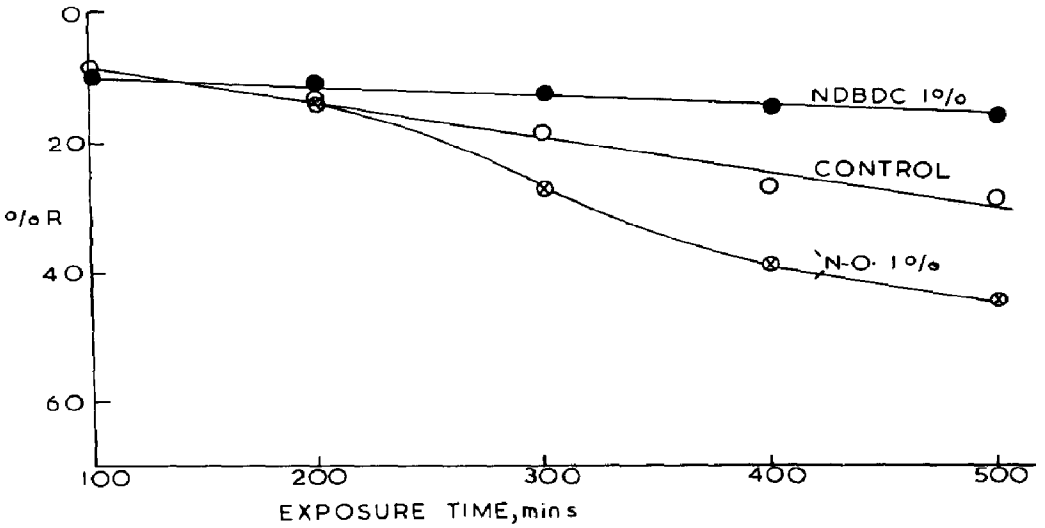


Fig. 7. Reflectance (%) *vs.* time of irradiation in a Xenotest-150 unit for prints of crystal violet lactone (1 g l^{-1}) colour: ○, alone; ●, 1 wt.% nickel dibutyldithiocarbamate; ⊗, 1 wt.% 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-*N*-oxy.

leuco colour former molecule as shown by the results in Fig. 8. In this case the residual leuco compound was determined using HPLC after irradiation in a toluene solution. Increasing the nickel complex concentration from 0.01 to 1 g l^{-1} resulted in a simultaneous improvement in the photostability of this compound.

The involvement of hydrogen peroxide and/or peroxides in the photo-oxidation of the dye is shown by the results in Fig. 9. Here the presence of the nickel complex completely inhibits peroxide formation during irradiation of solutions of the dye. Thus, the oxidation of the dye by peroxides

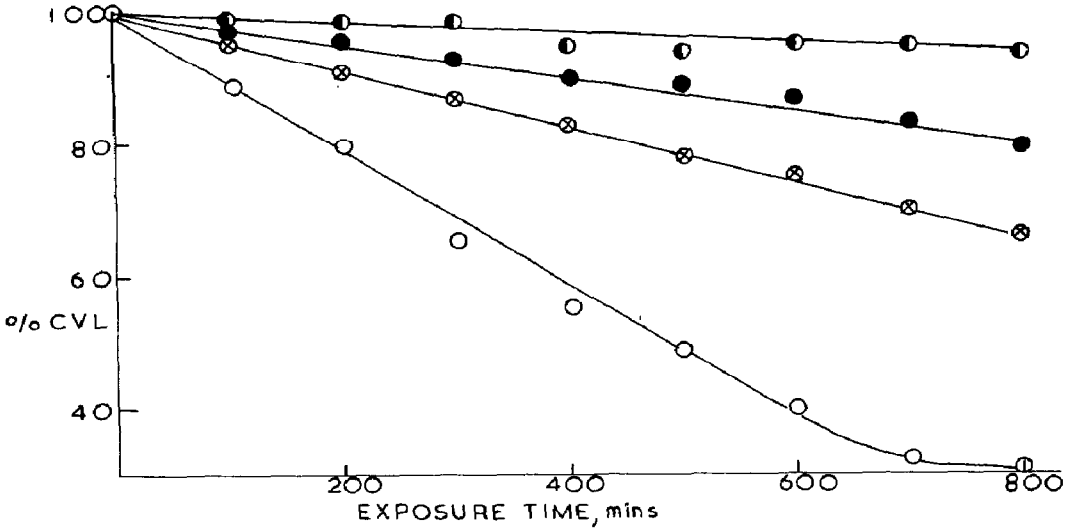


Fig. 8. Percentage crystal violet lactone (initial concentration, 1 g l^{-1}) remaining in toluene solution *vs.* irradiation time in minutes in a Xenotest-150 irradiation unit: ○, control solution; ◐, ● and ⊗, 1 wt.%, 0.1 wt.% and 0.01 wt.% nickel dibutyldithiocarbamate.

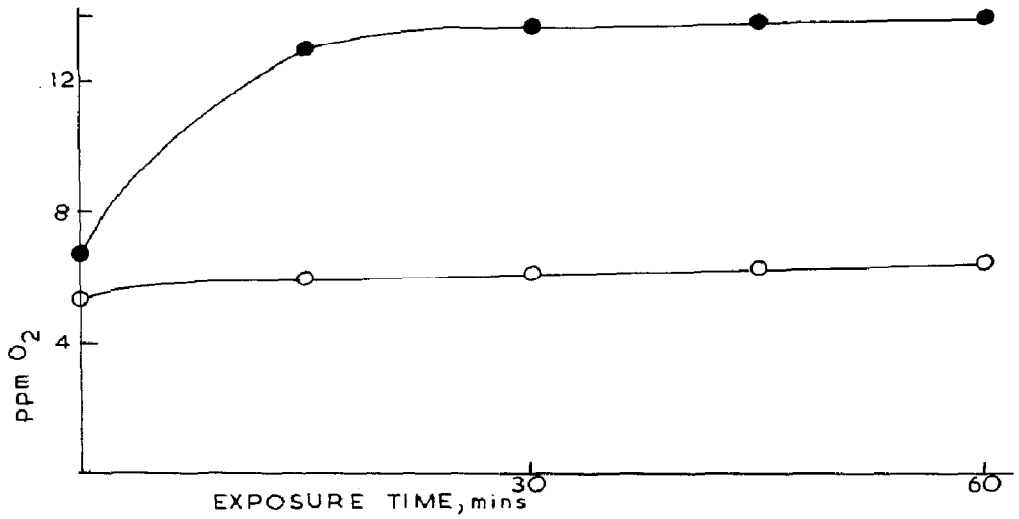


Fig. 9. Peroxide concentration *vs.* irradiation time in minutes in a Microscal unit for crystal violet lactone dye (10^{-4} M) in 67vol.%(acetic acid)–33vol.%chloroform in the absence (●) or the presence (○) of 10^{-4} M nickel dibutyldithiocarbamate.

shown in the latter part of Scheme 1 appears to be important under our experimental conditions.

Transient absorption spectra of the leuco crystal violet lactone in propan-2-ol and in a 50vol.%propan-2-ol–50vol.%(acetic acid) mixture are shown in Fig. 10. In the absence of acid only one transient is observed with a maximum at 380 nm and a half-life of 21 ms while in the presence of acid some long-lived absorption which is evidently associated with the flash-induced production of the dye colour is also observed at 605 nm. Both transients are quenched by oxygen, indicating the involvement of the triplet state of the colour former in free radical production as shown in Scheme 1. The transient absorption at 380 nm corresponds to the absorption spectrum of the crystal violet lactone free radical shown in Fig. 11. The latter was

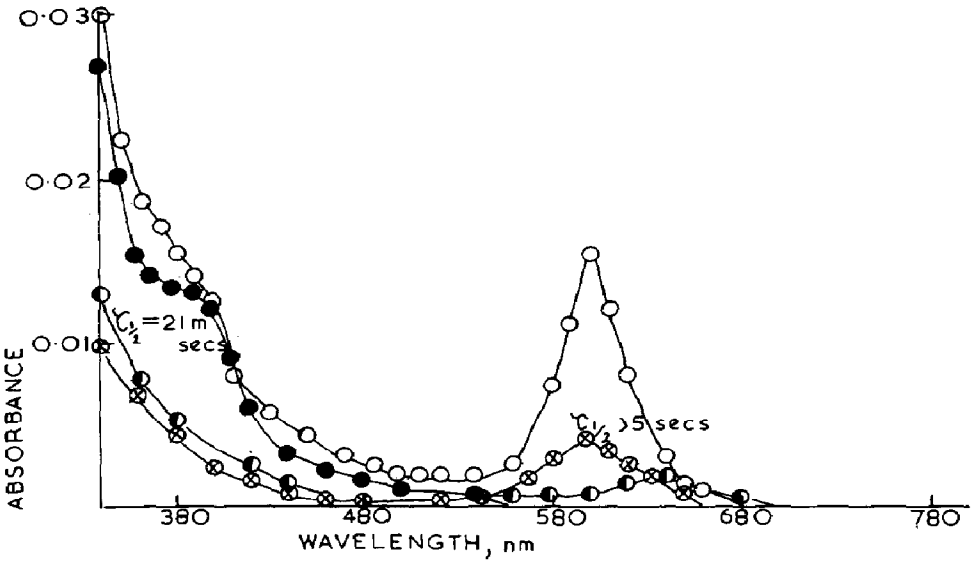


Fig. 10. End-of-pulse transient absorption spectra of crystal violet lactone (10^{-5} M) in 2-propanol (saturated with N_2 (●) or air (◐)) and in 50vol.%2-propanol–50vol.%(acetic acid) (saturated with N_2 (○) or air (⊗)).

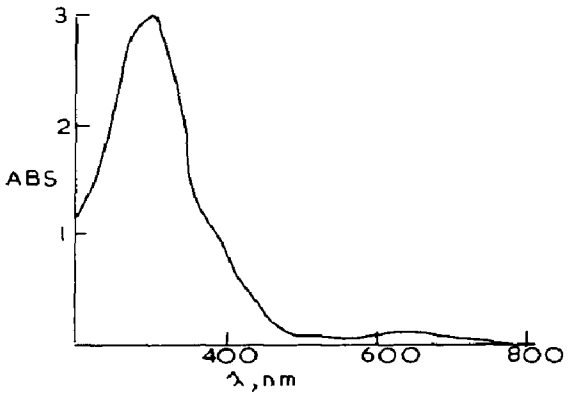


Fig. 11. Absorption spectrum of the leuco crystal violet lactone free radical in acetic acid produced by reduction using titanous chloride solution.

made synthetically in solution by reaction of the colour former with titanous chloride and had to be examined rapidly because of its instability in the presence of oxygen.

4. Conclusions

The results in this study clearly show that the light-induced fading of crystal violet lactone dye is an oxidative process involving peroxides, and essentially confirms the general mechanism in Scheme 1. This is supported by the observation that an effective peroxide decomposer, nickel dibutyldithiocarbamate, strongly inhibits dye fading. This may have practical implications in the stabilization of pressure-sensitive printing materials.

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