Dyes and Pigments **9** (1988) 319–327

Improvement in the Lightfastness of Dyed and Pigmented Materials—Part 2: Effect of Singlet Oxygen Quenchers on the Photostabilisation of Organic Pigments in Some Coating Films

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(Received 14 September 1987; accepted 27 October 1987)

ABSTRACT

The effect of some singlet oxygen quenchers on the photostabilisation of C.I. Pigment Red 3 and C.I. Pigment Red 49 in coating films prepared from cellulosic lacquer, alkyd resin and polyurethane-type paints was examined. The rates of photodegradation of the pigments were retarded by adding effective singlet oxygen quenchers, such as nickel diethyldithiocarbamate, nickel bis(dithiobenzil) and nickel bis(N-n-dodecylsalicylaldimine). The co-existence of an equal amount of the singlet oxygen quencher and a hindered phenol (good radical scavenger) was effective in improving the light resistance of the pigments, but the addition of a hindered phenol alone was not effective.

1 INTRODUCTION

The photofading of dyes and organic pigments is caused by mechanisms such as oxidation, reduction and photo-isomerisation. In general, it is presumed that the oxidation reaction plays an important role in the photofading. Previous reports[1-7] suggest that the oxidation by singlet oxygen ($^1O_2$) is one cause of such photofading, as well as the autoxidation which is concerned with free radicals due to oxygen molecules present in the air (triplet oxygen, $^3O_2$). This suggestion is based on an assumed mechanism by which the singlet oxygen molecules, produced when the energy of a dye or

Dyes and Pigments 0143-7208/88/$03·50

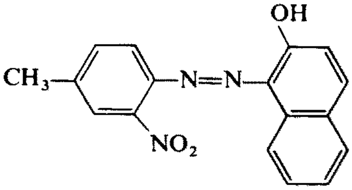
pigment existing in the photo-excited triplet state migrate to the oxygen molecules in the ground state, function as a reaction-activating species.[1,3,7-13] Recently, much attention has been paid to this mechanism from the viewpoint of the prevention of photodegradation. In Part 1 of this study it was shown how singlet oxygen quenchers could be utilised for improving the light resistance of cellulose acetate films containing some dyes.[14]

On the other hand, there have been numerous studies on the photodegradation or photostabilisation of coating films and polymers containing organic pigments. Many of these studies have been concerned with the photostabilisation of the substrates by antioxidants (hindered phenols and amines) and UV-absorbers,[15-22] and to the relevance of the singlet oxygen mechanism to plastic polymers.[22-29] No studies have been reported concerning the action of singlet oxygen quenchers on organic pigments in coating films and we describe here the additive effects of singlet oxygen quenchers on the light-stability of some red organic pigments in some coating films.

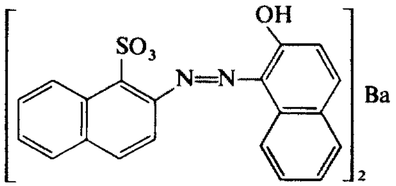
2 EXPERIMENTAL

2.1 Materials

The organic pigments C.I. Pigment Red 3 (Lake Red 4R, C.I.12120) and C.I. Pigment Red 49 (Lithol Red, Ba-lake, C.I.15630) were obtained from a commercial source. The formulae of these materials are shown in Fig. 1.



C.I. Pigment Red 3
(C.I. 12120)



C.I. Pigment Red 49
(C.I. 15630)

Fig. 1. Pigments used in this study.

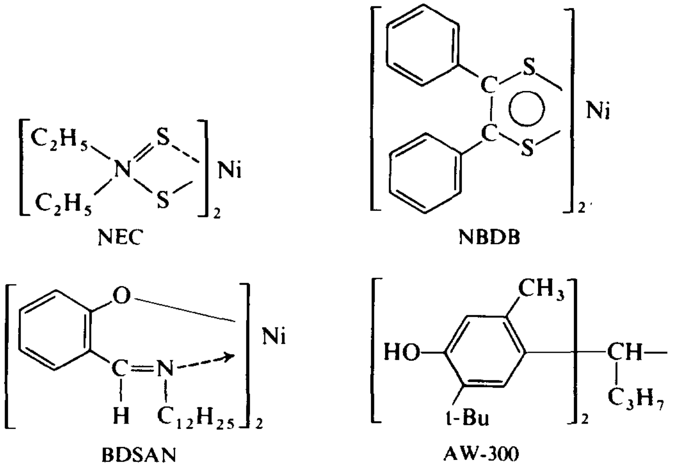


Fig. 2. Singlet oxygen quenchers and antioxidant used in this study.

As the resin for coating materials, a clear cellulosic lacquer (manufactured by Nippon Paint Co. Ltd; N-2200), an alkyd resin (sunflower oil denatured with phthalic acid; Becksol J-557; Dainippon Ink Co. Ltd) and clear two-component polyurethane (Nippon Paint Co. Ltd) containing no commercial additives were used.

2.2 Singlet oxygen quenchers and antioxidants (Fig. 2)

Nickel(II)bis(dithiobenzil) (NBDB) was synthesised from benzoin according to the literature;[30] m.p. 294–295°C. Nickel(II)bis(*N*-*n*-dodecylsalicylaldimine) (BDSAN) was synthesised from salicylaldehyde and *n*-dodecylamine according to the literature;[31] m.p. 96–97°C. Nickel(II)diethyldithiocarbamate (NEC) was supplied by Oouchi Sinko Co. Ltd (Japan) and was used without further purification.

The antioxidant, 4,4′-butylidene bis(6-*t*-butyl-*m*-cresol) (Kawaguchi Chemical Co. Ltd; AW-300) was used without further purification. The UV-absorber, 2-(2′-hydroxy-3′-*t*-butyl-5′-methylphenyl)-5-chlorobenzotriazole, known commercially as Tinuvin 326, was supplied by Ciba–Geigy Ltd, Japan.

2.3 Preparation of coating films

A clear cellulose lacquer (100 g), C.I. Pigment Red 49 (8 g), an additive (0·5–2·0 wt% based on the film-forming ingredients) and lacquer thinner (40 g) were placed in a ball-mill, and then dispersed for 20 h. The dispersion was applied to soft steel sheets (JIS, G3141, 7 cm × 15 cm × 0·08 cm) and was coated using a film-applicator. The coating films (20–30 μm thickness) were prepared by drying at room temperature for a week.

Coating films from alkyd resin type paints were prepared by ball milling for 48 h a mixture of 100 parts of Becksol J-557, 12·6 parts of an organic red pigment, 0·3–2·0 parts of a light stabiliser, 30 parts of a solvent (aliphatic hydrocarbon), 0·8 parts of 6% aqueous cobalt naphthenate and 1·2 parts of 2·4% aqueous lead naphthenate. The mixture was applied to soft steel sheets, and coated in the same manner described above. The coating films were dried for a week at room temperature.

Polyurethane paint derived from clear polyurethane, C.I. Pigment Red 49 and the additives (0·5–1·0 wt%) was sprayed onto a soft steel sheet using an air spray gun.

Pale colour films (red pigment/$TiO_2 = 1:1$, 4 g of each) containing titanium oxide (hydrochloric acid process; CR-93, Ishihara Sangyo Co. Ltd) were also prepared by the same treatment.

2.4 Photofading and determination of colour difference

The coating films were exposed in a fadeometer (Toyo Rika Ltd) employing an ultraviolet carbon arc lamp filtered by a quartz envelope (55°C; 30% relative humidity). Films were also exposed in a sunshine carbon arc type weather meter (Suga Test Instruments Co. Ltd) employing a Pyrex filter envelope (60°C, 75% relative humidity). A water spray cycle was run at regular time intervals.

The rates of photodegradation of the pigments in the coating films were monitored by changes of colour difference ΔE^*ab using a colour difference meter (Nippon Densyoku SZ-Σ80 apparatus).

3 RESULTS

3.1 Exposure of cellulosic lacquer films

Coating films derived from cellulose lacquer type paints were exposed to a carbon arc light for 60–120 h in a fadeometer, and the changes in the colour occurring during exposure were determined from the colour difference ΔE^*ab. Figure 3 shows the measurement results.

The films with 0·5% of NEC, NBDB and BDSAN had a colour difference less than that of the standard film with no additives by 20–40%, respectively, which indicates a high light-stabilising effect. The dependence on the amount of addition was not large, and for light stabilisation, an amount of about 0·5% was effective. The coexistence of an equal amount of NBDB and AW-300 was effective for further improving the light resistance.

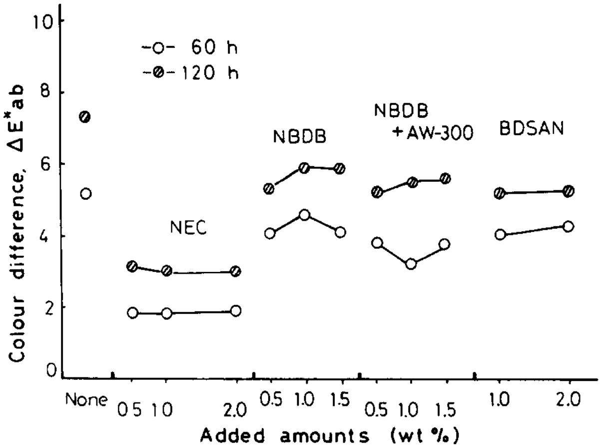


Fig. 3. Effect of various additives on the photostabilisation of C.I. Pigment Red 49 in cellulose lacquer-coating films; exposure with carbon arc lamp in a fadeometer, initial concentration of the pigment 8 wt%.

Similar experiments for pale-colour films (C.I. Pigment Red 49/TiO_2 = 1:1, 4 g of each) containing titanium oxide were carried out, and the results are shown in Fig. 4. The effect of additives on the photostabilisation of C.I. Pigment Red 49 showed similar trends to those found in the absence of titanium oxide.

3.2 Exposure of alkyd resin type films

Coating films prepared from alkyd resin paints of 100 parts of Becksol J-557, 12·6 parts of C.I. Pigment Red 49, 0·3–2 parts of the additive, 30 parts of a

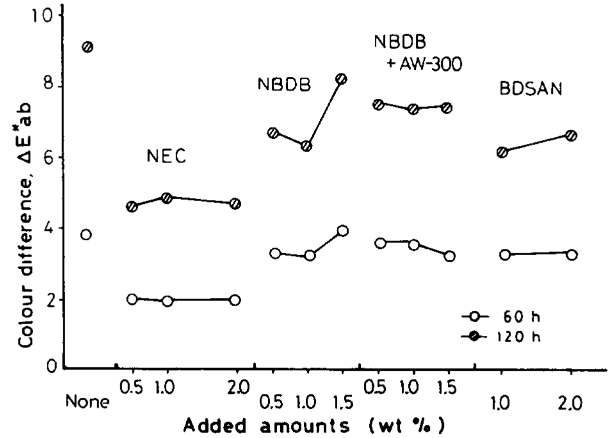


Fig. 4. Effect of various additives on the photostabilisation of C.I. Pigment Red 49 in cellulose lacquer-coating films containing titanium oxide; exposure with carbon arc lamp in a fadeometer, initial concentration of the red pigment 4 wt%, titanium oxide 4 wt%.

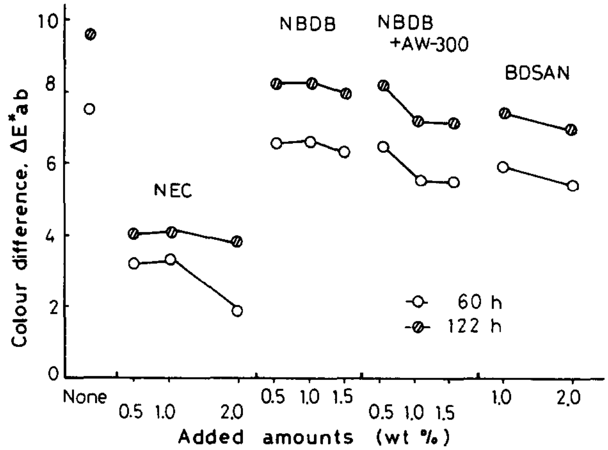


Fig. 5. Effect of various additives on the photostabilisation of C.I. Pigment Red 49 in alkyd resin-coating films; exposure with carbon arc lamp in a fadeometer, initial concentration of the pigment 12·6 wt%.

solvent, and drying agents (cobalt- and lead-naphthenates) were examined in a similar manner to that described above for cellulose lacquer films. Figure 5 shows the results of the films light-exposed in a fadeometer. The results indicate that the addition of NEC, NBDN and BDSAN, which are light stabilisers, having a deactivating effect on singlet oxygen, is effective in reducing Δ*E***ab*, thus resulting in light stabilisation.

The coating films of the alkyd resin type were also exposed to carbon arc light in a sunshine weather meter. Figure 6 shows the measurement result under these conditions. In this case, the dependence on the added amounts was larger than in the case of light-exposure in a fadeometer. The addition of

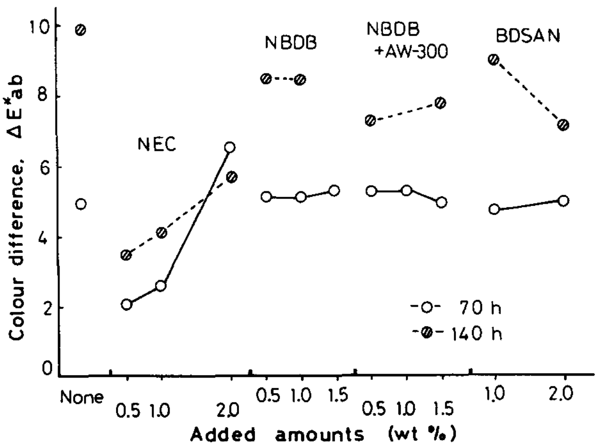


Fig. 6. Effect of various additives on the photostabilisation of C.I. Pigment Red 49 in alkyd resin-coating films; exposure in a sunshine carbon arc type weather meter, initial concentration of the pigment 12·6 wt%.

TABLE 1
Effects of Additives on the Photostabilisation of C.I. Pigment Red 3 in Cellulosic Lacquer Type and Alkyd Resin Type Coating Films[a–c]

Resin	*TiO_2*[d]	*Additives*				
		NEC	*NBDB*	*AW-300*	*NEC + AW-300*	*Tinuvin-326*
Cellulose lacquer		+	+	−	+	+
	○	+	+	±	+	±
Alkyd		+	+	−	±	±
	○	±	+	−	+	±

[a] Concentration of the pigment was 8 wt% on the basis of the film-forming ingredients. The respective additive was at 0·5 wt%.
[b] The coating films were exposed for 120 h in a fadeometer.
[c] After the exposure, colour difference ΔE^*_{ab} was measured, and the value of $A = \Delta E^*_{ab}$ (sample/ΔE^*_{ab} (standard) was then calculated: $+, A < 0{\cdot}85$; $-, A > 1{\cdot}15$; $\pm, 0{\cdot}85 \leqslant A \leqslant 1{\cdot}15$.
[d] In the cases marked ○, C.I. Pigment Red 3 (4 g) and TiO_2 (4 g) were contained in the films.

0·5 wt% of NEC in the film-forming ingredients was most effective, but the stabilising effect decreased with increasing amounts.

Further experiments for pale-colour films containing titanium oxide in this type of paint were carried out, and the light-stabilising effect on C.I. Pigment Red 49 by the additives was also apparent.

The use of C.I. Pigment Red 3 as the organic red pigment was also examined. The effects of various additives on the photostabilisation of C.I. Pigment Red 3 in coating films prepared from a cellulosic lacquer paint and an alkyd resin paint are summarised in Table 1. In this case, the addition of NEC and NBDB resulted in enhanced light stability of the pigment. The use of a combination of NEC and AW-300 was also very effective, although AW-300 alone did not have any effect on the lightfastness. On the other hand, the addition of Tinuvin-326, a UV-absorber, showed a slight stabilising effect.

3.3 Exposure of polyurethane coating films

For clear two-component polyurethane, a polyol and an isocyanate prepolymer (Polyuremytilac clear), which was supplied by Nippon Paint Co. Ltd, Japan, were used. The polyurethane coating films containing C.I. Pigment Red 49 (8 wt%) and various additives (0·5–1·0 wt%) were exposed to an ultraviolet carbon arc lamp in a fadeometer employing a Pyrex filter envelope. After exposure for 200 and 400 h, colour difference ΔE^*ab values and gloss properties of the film surfaces were measured. The results are summarised in Table 2.

TABLE 2
Effect of Additives on the Photostabilisation of C.I. Pigment Red 49 in Polyurethane Coating Films[a]

Additives	*Added amounts (wt%)*	*Colour difference*		*Gloss retention*[b] *(%)*
		*ΔE*ab*	*Ratio*	
None		15·59	1·00	84·76
NEC	0·5	12·33	0·79	91·61
NEC	1·0	12·86	0·82	86·54
NBDB	0·5	11·20	0·72	86·23
NBDB	1·0	12·00	0·77	85·97
NBDB + AW-300	0·5 + 0·5	9·12	0·58	82·75
NBDB + AW-300	1·0 + 1·0	10·66	0·68	92·16
BDSAN	0·5	11·40	0·73	90·07
BDSAN	1·0	12·24	0·78	86·68

[a] Concentration of the pigment was 8 wt% on the basis of the film-forming ingredients. These films were exposed for 200 h with a carbon arc lamp in a fadeometer.

[b] Shows a % of the retained gloss value after the exposure.

From the table, it is concluded that the light-stabilising effect resulting from the additives was also obtained in the case of polyurethane coating films containing the red pigment. That is, the additives act not only by enhancing the light resistance of the colour, but also give improvement of the gloss preservation. Also, they do not have a harmful influence on other film properties such as those shown by the cross-cut and cracking tests.

The above additives are pale green or brown in colour. Accordingly, it is necessary that they are not used excessively in paints containing pigments of pale colour, such as yellow and orange, at low concentration. However, in the case of red coatings, as studied in this present work, and in coatings of pink, violet, blue, green, brown and black colours, the addition of about 0·1–0·5 wt% based on the film-forming ingredients is effective. Such an amount is relatively small, and does not result in changes in the colour of the films.

4 CONCLUSIONS

The contribution of singlet oxygen to the photodegradation of some dyes and organic pigments in solution has been investigated by several authors. However, few studies involving the use of singlet oxygen quenchers as a means of improving the lightfastness of coloured materials have been made. In this paper we have reported the effect of singlet oxygen quenchers on the photostabilisation of organic red pigments in some typical coating films, such as are frequently used in industrial practice.

Owing to specific interactions between the pigment and substrate, the photodegradation reaction of the pigment will probably be more complicated than in solution. For a fuller discussion with regard to these mutual interactions, more detailed investigations are necessary. However, a novel approach for improving the lightfastness of organic pigments in such systems is indicated by the results obtained in this present investigation.

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