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REVIEW

The Effect of Additives on the Photostability of Dyed Polymers

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1 INTRODUCTION

Two principal types of photodegradation can take place when solar radiation falls on a dyed polymer: (i) change in shade and/or depth of shade of the colorant and/or (ii) chemical degradation of the substrate.

Many factors influence the lightfastness of dyes on polymers, and these principally include the chemical structure of the dye, the physical state of the dye within the fibre, the chemical structure of the substrate, additives within the substrate, atmospheric composition (oxygen, water and/or contaminants), ambient temperature and the spectral distribution of the incident light. Similar parameters influence the concomitant photochemical degradation of the polymer host.

The chemical changes that molecules undergo following absorption of solar radiation is a field of great interest to organic chemists and over the last 40 years significant progress has been made in our understanding of the photochemistry of dyes and polymers and the mechanisms of their photodegradation.

To reduce the undesirable degradation effects of solar radiation on dyed polymeric materials, several approaches have been considered ranging from deliberate structural modification of dyes to the use of protective agents

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of various kinds. A variety of additives have been developed commercially which can be used either before, during or after the dyeing process or incorporated in the polymer at the processing stage of manufacture. Such additives may protect the dye, the polymer substrate or, ideally, both. The overall extent of protection of a dyed polymer by such an additive is of course influenced by the rate of physical and chemical loss of the additive during the lifetime of the material.

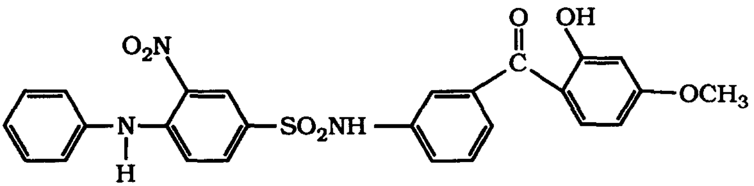
Although considerable progress has been made in the use of stabilisers over the past decade, many problems still remain. This paper reviews briefly the more significant developments that have been made in recent years in the use of additives for improving the lightfastness of dyed polymers and for convenience the subject material is divided into the different mechanistic classes of additive and the stabilisation methods employed. However, it should be noted that the rigorous classification of stabilisers according to mechanism is fraught with difficulty, as in many cases the exact mechanisms of stabilisation are not known, and often a stabiliser can exert its effect in more than one way.

2 UV ABSORBERS

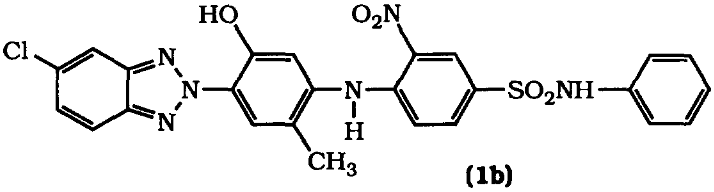
A UV absorber is a molecule that is incorporated within a host polymer and which absorbs ultraviolet light efficiently and converts the energy into relatively harmless thermal energy without itself undergoing any irreversible chemical change, or inducing any chemical change in the host molecules. Typical UV absorbers are the 2-hydroxybenzophenones, 2-hydroxyphenylbenzotriazoles and 2-hydroxyphenyl-*s*-triazines, which convert electronic excitation energy into thermal energy via a fast, reversible, intramolecular proton transfer reaction.

UV absorbers are technically important for preventing photodegradation of polymers with or without organic pigments. Dyes containing a built-in ultraviolet absorber moiety such as 2-hydroxybenzophenone have been used as reactive dyes for cotton [1], and dyes containing a 2,4-dihydroxybenzophenone residue have been described for polypropylene fibres containing nickel [2,3]. Similar approaches have been used for cationic dyeing, and for example Sekimoto *et al.* used 2,2′-dihydroxy-4,4′-dimethoxybenzophenone on the cationically dyed poly(*m*-phenyleneterephthalimide) fibres, to obtain improved colour yields and lightfastness [4].

More recently, Freeman and co-workers have investigated an interesting approach to the synthesis of lightfast disperse dyes, where the dye contains a built-in photostabiliser moiety of the benzophenone (**1a**) or benzotriazole types (**1b**) [5–7].

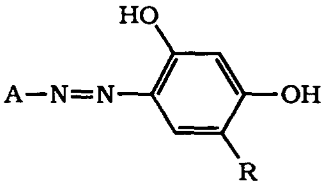


(1a)

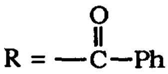


(1b)

Along similar lines, Rajagopal and Seshadri prepared azo dyes of general structure (**2**) for cotton, wool and leather, using 2,4-dihydroxybenzophenone as coupling component [8]. These dyes contain the *ortho*-hydroxybenzophenone moiety, but as part of the dye itself. They observed that the dyeings were generally deeper in shade and had better lightfastness than those from dyes (**2**; R = H) based on resorcinol as coupling component.



A = sulphanilic acid, naphthionic acid, *p*-aminobenzenesulphonic acid

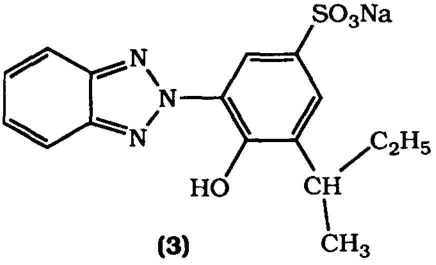


$R = -\overset{O}{\overset{\|}{C}}-Ph$

(2)

Suitably tailored UV absorbers have been described for application to fibres during or after the dyeing process. Benzotriazoles were used successfully with disperse dyes on polyester [9,10], nylon [11–15], cotton [16] and on wool [14,17–19].

Reinert developed a method for increasing the photostability of anionic dyes on wool fibres, which involved first dyeing the wool in the presence of a UV absorber such as (**3**) then treating with an oxidative bleaching agent (H_2O_2) and finally treating with a reducing bleaching agent ($NaHSO_3$) [20].



(3)

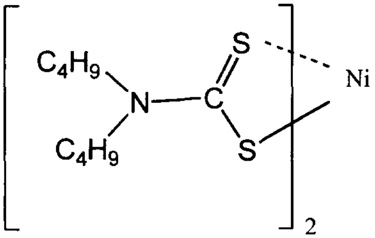
Benzotriazoles have been used successfully as stabilisers for disperse dyes in coating films prepared from a cellulosic lacquer and an alkyd resin [21] and for anionic reactive dyes in protein fibers [22].

Finally, there have been reports of the use of commercial UV absorbers with quinone dyes [23], quinophthalone dyes [24] and bis(indolylazo)triazolium dyes [25] on polyester to produce lightfast fabrics suitable for automobile interiors.

3 FREE RADICAL SCAVENGERS/HYDROPEROXIDE DECOMPOSERS

There is much evidence to show that the vast majority of dye and polymer photodegradation pathways are oxidative in nature, and given that molecular oxygen in its ground state is a triplet it is not surprising that free radical species play an important role in initiation and propagation of the complex reactions involved. For example, one radical may abstract hydrogen from the polymer molecule to generate a new radical, which on reaction with oxygen will form a peroxide radical. This itself may abstract hydrogen to produce the polymer hydroperoxide and yet another radical. Hydroperoxides are susceptible to thermal and photochemical homolytic cleavage giving two radicals, HO· and Polymer-O·, and thus they play a major role in accelerating and propagating subsequent degradation processes. Clearly then any species that scavenges free radicals or reacts with hydroperoxides in such a way that it neutralises their propagating effect will be a useful photostabiliser.

Although many radical-scavenger antioxidants are known, most of these are suitable only for thermal stabilisation and are unsuitable for photochemical systems. Photostabilising scavengers are largely restricted to transition metal chelates, especially nickel dialkyldithiocarbamates, e.g. (**4**), and the hindered amine light stabilisers (HALS), e.g. 2,2,6,6-tetramethylpiperidine (**5**). It is believed that certain UV absorbers (e.g. 2-hydroxybenzophenones) can also play a role as scavengers. The HALS are particularly important stabilisers they act not only as scavengers (via their *N*-oxy derivative formed *in situ* by oxidation), but they also directly react with and decompose hydroperoxides.



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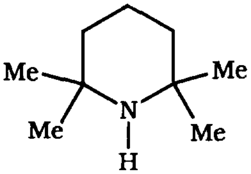

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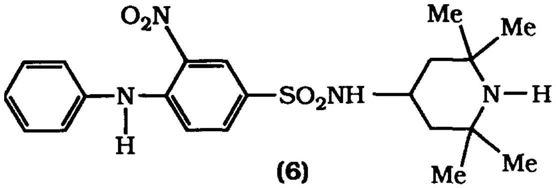
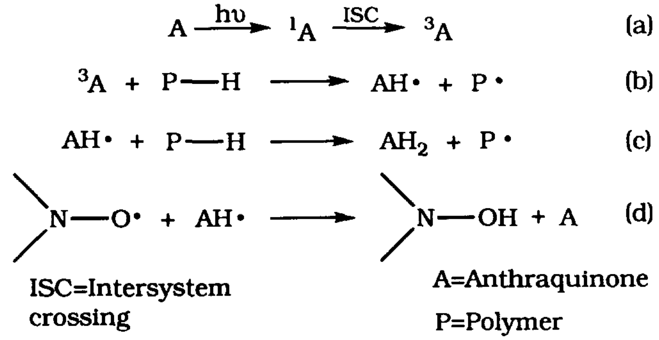

(6)

Occasionally dye fading may be attributable to reduction of the dye chromophore, at the expense of oxidation of the polymer host. In such cases, antioxidants may still have a beneficial effect, and this was demonstrated by Allen *et al.* [26] with disperse anthraquinone dyes in epoxy resin films. They found that the *N*-oxy radicals from HALS were the most efficient at inhibiting the photoreduction of the anthraquinone system (A) to the *leuco*-anthraquinone (AH_2) (Scheme 1). It was suggested that this effect was due to the ability of the *N*-oxy radical to react with semiquinone radical (AH·), which is first formed by hydrogen atom abstraction by the excited triplet state of the dye (Scheme 1). In this process the anthraquinone dye is regenerated and a hydroxylamine is formed. The effects of two such antioxidants are shown in Fig. 1.

The efficiency of compounds that generate *N*-oxy radicals is due, according to the authors, to a regenerative process involving peroxy radicals (Scheme 2). These are easily formed through processes (b) and (c) Scheme 1, followed by reaction with oxygen (Scheme 2).

In the case of the HALS Tinuvin 770 [bis(2,2,6,6-tetramethyl-4-piperidinyl) sebacate] (Fig. 1), its stabilising effect is also due to the formation of a nitroxyl radical (Scheme 3a). However, the presence of the dye seems to inhibit this process, its efficiency being highly reduced during the last stages of irradiation probably due to a hydrogen atom abstraction process (Scheme 3b). Tateoka *et al.* have suggested the use of hindered amines light stabilisers to increase the light stability of photochromic spirobenzoxazine dyes for


$$A \xrightarrow{h\upsilon} {}^1A \xrightarrow{ISC} {}^3A \quad (a)$$

$$^3A + P{-}H \longrightarrow AH\bullet + P\bullet \quad (b)$$

$$AH\bullet + P{-}H \longrightarrow AH_2 + P\bullet \quad (c)$$

$$>N{-}O\bullet + AH\bullet \longrightarrow >N{-}OH + A \quad (d)$$

Scheme 1

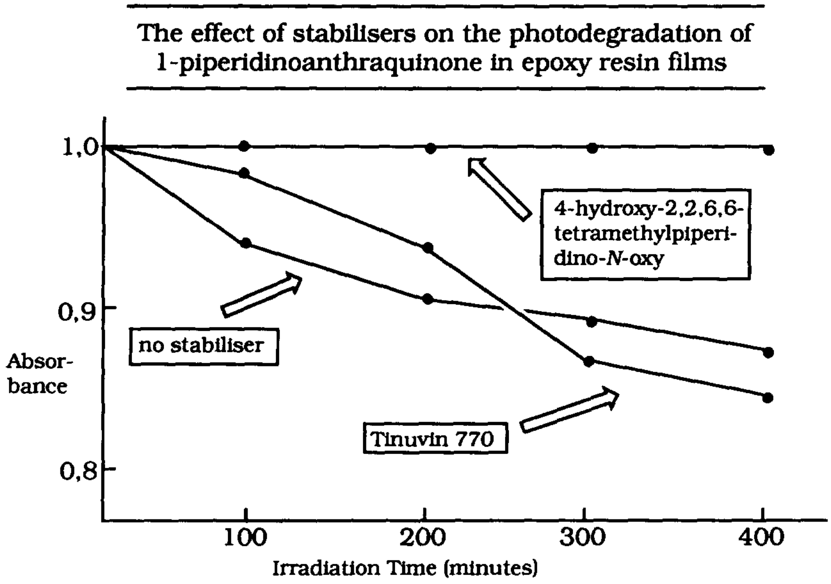
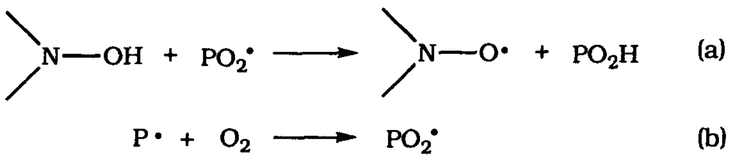
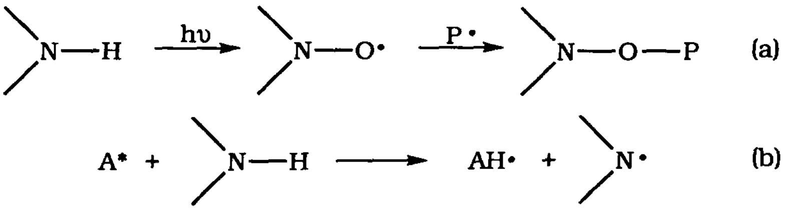


Fig. 1.



Scheme 2



Scheme 3

automotive and building window materials [27] and Iwata *et al.* were able to improve the lightfastness of dyed polyurethane fibers by incorporating hindered amines and hindered phenols during the manufacture process [28].

Freeman and co-workers when designing lightfast dyes for automotive fabrics, prepared several disperse dyes containing a built-in hindered amine residue (**6**) and they were shown to have improved lightfastness [5,6,29].

Recently, Ligner and Hess studied the interactions of HALS type radical scavengers with automotive clear coats and discussed some of the possible transformations that can occur after they are incorporated into the polymer [30].

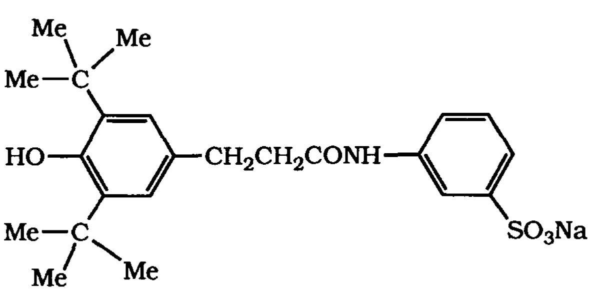
Allen confirmed the photostabilising effect of nickel salts, NiDBDTC (nickel dibutyldithiocarbamate) and Negopex B [nickel bis(*syn*-undecyl-2-hydroxy-4/5-methylphenylketoxime)] [26], whose action to trap HO· and PO· radicals is known [31–33]. The authors suggested that the higher efficiency of Negopex B, besides acting as radical scavenger, may be due to its ability to quench the triplet state of the dye.

Chakraborty and Scott studied the effect of UV-531 (2-hydroxybenzophenone), which is also a HO· and PO· radical scavenger [34,35], having observed an increase on lightfastness of the dyes under consideration and suggested a mechanism on which the destruction of the stabiliser occurs. Shah and Jain improved the lightfastness of solubilised vat dyes on nylon 66 using hydroquinone as aftertreatment [36]. The authors concluded that the observed increase in lightfastness was not due to a UV filter effect, but rather a consequence of the antioxidant action of hydroquinone, which is converted oxidatively into benzoquinone, so delaying dye fading.

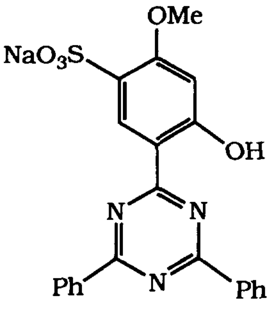
The hydroquinone antioxidative action was later confirmed on nylon 6 using solubilized vat dyes [37].

The effects of other radical scavengers on dye photostabilisation have also been studied. Allen *et al.* examined the behaviour of potassium thiocyanate on the presence of anthraquinone dyes in solution [38]. Its action as hydroxyl radical trap is known [39] and the degree of photofading was reduced by *ca* 50%.

Although hindered phenols are not usually effective antioxidants in photochemical systems, recently Reinert and Fuso improved the lightfastness of azo dyes on polyamides using acid-dyeable phenols of this type in the aqueous dyebath [40]. For example, the phenols (**7**) and (**8**) were applied simultaneously to the fibre. In this case (**8**) would be acting as a UV absorber. Subsequently Reinert described a method for thermal and photochemical stabilisation of nylon carpeting for automobiles dyed with 1:2 metal–complex dyes using mixtures of a hindered phenol, a UV absorber and a copper complex [41].



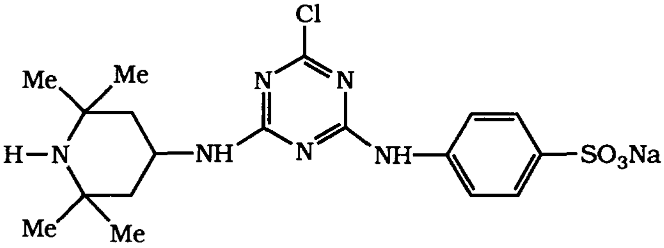
(7)



(8)

Takuma has also suggested the use of various hindered phenols as stabilising agents for cyanine dyes in optical recording material [42–44].

Triazine soluble HALS derivatives (9) have also been used to increase the photochemical stability of dyes on polyamide [45] and on wool [46].



(9)

Kuramoto *et al.* examined the effect of the antioxidant AW300 [4,4′-butylidene bis(6-*t*-butyl-*m*-cresol)] when applied to cellulosic lacquer paints and alkyd resin paints [21]. They concluded that the addition of AW300 and NEC (nickel diethyldithiocarbamate) resulted in synergistic enhanced light stability of the pigment, although AW300 alone did not have any effect.

4 SINGLET OXYGEN QUENCHERS

The involvement of singlet oxygen ($^1\Delta g$) in the degradation reactions of dyes and polymers is now well accepted, although the relative significance of this mechanism in comparison with free radical oxidative pathways is far from clear, and will vary from system to system. Nevertheless, in suitable cases known singlet oxygen quenchers can have a definite photostabilising effect both on dyes and on the polymer substrate. The situation is complicated, however, by the ambiguous characteristics of such quenchers, and one can always suggest alternative mechanisms for their beneficial effect. For example, nickel chelates are singlet oxygen quenchers but also can act as radical scavengers. Similarly, tertiary amines which quench singlet oxygen effectively can also interact with excited states, and in particular as we have seen HALS are potent hydroperoxide scavengers.

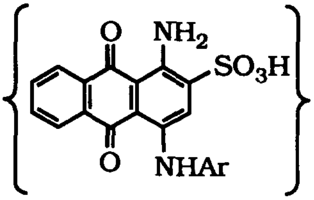
This ambiguity was well demonstrated in the anaerobic photofading of anthraquinone dyes and Allen *et al.* studied the effect of various additives on the photofading of anthraquinone dyes in N_2-saturated solution (Table 1) [38]. The stabilising influence of DABCO, a well known tertiary amine singlet oxygen quencher, was at first very surprising given the anaerobic nature of the system. However, as DABCO is a particularly nucleophile amine and, according to the authors, the photostabilising effect is most likely to be due to its ability to quench the excited states of the dye either through electron transfer or collisional quenching. A similar stabilising effect by ethylenediamine was also observed (Table 1).

Allen *et al.* also studied the influence of DABCO on the photofading of anthraquinone disperse dyes in epoxy resin films [26]. The authors concluded that $^1O_2$ plays an important role in the irreversible photofading of this type of dye.

Other oxygen singlet quenchers have been examined as photostabilisers. Kuramoto examined the effect of nickel salts on the photodegradation of direct (C.I. Direct Red 39) and quinophthalone (C.I. Solvent Yellow 33) dyes in

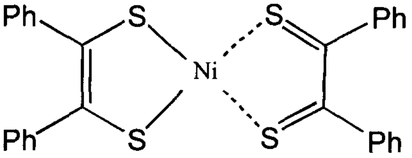
Table 1

Effect of sensitisers and stabilisers on the photofading of the dye in N_2-saturated 3:2v/v propan-2-ol:H_2O mixtures

Additive (1×10^{-3} M concentration)		% Fading after 10 photoflashes
Control		40
DABCO		29,3
Ethylenediamine		22,4
Potassium thiocyanate		23,6
Benzophenone		99,2
o-phenylphenol		19,5
p-phenylphenol		23,0
Diphenyl		78,3
Tetracyanoethylene		4,6
4-hydroxy-2,2,6,6-tetramethyl-*N*-oxypiperidine		2,9

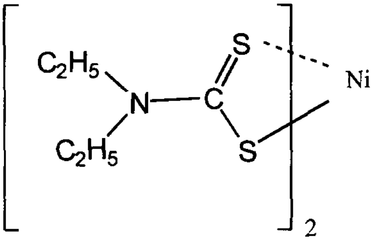
cellulose acetate films [47]. He observed that whilst addition of 2,6-di-*t*-butyl-4-methylphenol (peroxide radical scavenger) gave only a slight protection against photodegradation, the lightfastness was improved significantly in the presence of antioxidants such as NBDB [nickel(II)bis(dithiobenzil)] **(10)**, nickelbis(mesitilenesulphonate) and nickel dialkyldithiocarbamates. It is unclear, however, if these are quenching singlet oxygen or acting as radical scavengers, or both.

The same author demonstrated the effect of nickel complexes (**10**, **11** and **12**) on the photostabilisation of organic pigments (C.I. Pigment Red 3 and C.I. Pigment Red 49) in cellulosic lacquer, alkyd resin and polyurethane-type paints [21]. The light stability of the pigments increased with the addition of nickel salts or through the combined action of these salts and a hindered phenol (peroxide radical scavenger). However, the addition of a hindered phenol alone was not effective.



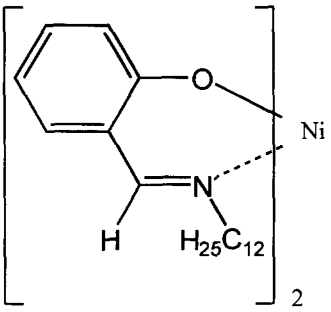
NBDB

(10)



NEC

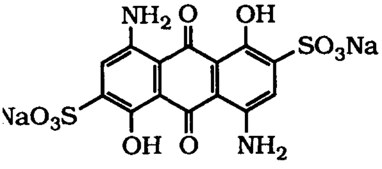
(11)



BDSAN

(12)

Oda and Kitao observed an improvement in the lightfastness of sulphonic acid dyes as their nickel salts, in solution and on silica gel, compared to their corresponding sodium salts [48]. Dyes examined were (**13**) and (**14**). The improved lightfastness was similar to that resulting from the addition of nickel salts of *p*-toluenesulphonic acid to the sodium salts of the dyes. The authors concluded that the nickel sulphonates were acting as $^1O_2$ quenchers.



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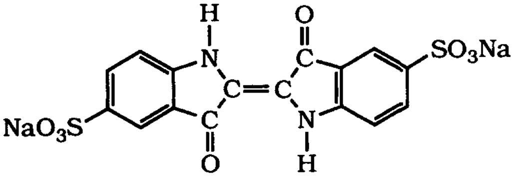


(14)

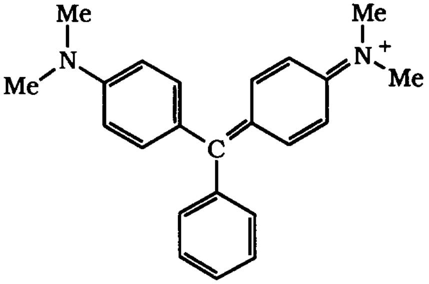
Kabiki obtained better lightfastness of reactive dyes on wool using tertiary amines (dimethylethanolamine) in the dyebath [49], and this may have been due to the quenching of $^1O_2$. However, reductive fading of dyes on wool is more usually observed.

5 OTHER ADDITIVES

Because of the commercial incentive to improve the photostability of dye–polymer systems, innumerable additives have been examined over the years on a purely empirical basis, and as a consequence interesting examples of enhanced lightfastness have emerged where the mechanism of stabilisation by the additive is far from clear. More recent examples of such investigations are summarised collectively in this section.

Allen *et al.* studied the influence of *o*- and *p*-phenylphenol on the lightfastness of commercial anthraquinone dyes in anaerobic solution [38]. The effect of these compounds is interesting since they are used as carriers in the dyeing of polyester fibres, and some disperse dyes have their light fastness impaired by carriers. In this case, they were protective (Table 1) and the authors suggested that this effect may be due to a screening effect (these carriers have high absorbances in the UV) since their ability to act as radical traps would be expected to be low.

Triphenylmethane cationic dyes, formerly used on protein and cellulosic polymers, are now used on polyacrylonitrile substrates because of their acceptable lightfastness properties on these substrates [50]. The photostability of triphenylmethane dyes is particularly sensitive to their environment (substrate, oxygen and water). Enmanji improved the lightfastness of malachite green (**15**) using caffeine (**16**) and the lightfastness of methylene blue (**17**), a thiazine dye, by treatment with DNA and *β*-cyclodextrin [51,52].



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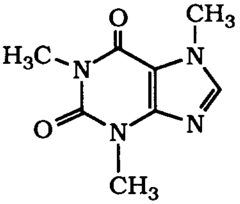
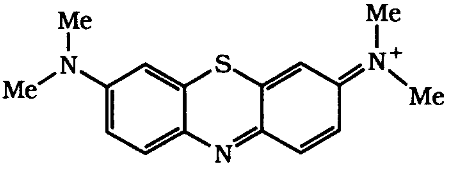


(16)



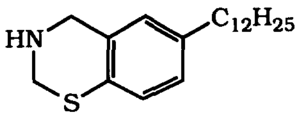
(17)

The use of *β*-cyclodextrin in association with water soluble dyes to give ink-jet recording inks with excellent lightfastness has been proposed [53].

It has been reported that phenothiazine compounds can be used to prevent discoloration of inks, dyes and colour photographic materials [54], and in association with fluoran leuco dyes to produce light fast images for thermal recording materials [55].

Sato *et al.*, using cyanine dyes in conjugation with metal complexes improved the dye lightfastness in optical recording medium [56,57].

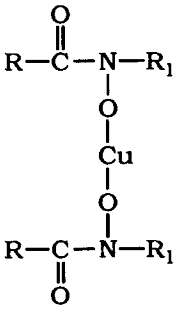
Recently, Kaneko suggested the use of alkyl metal sulphates [58] and hydrobenzothiazine derivatives (**18**) [59] for improving colour image stability and lightfastness in inks and colour photographic materials.



(18)

The electron-trapping ability of tetracyanoethylene is known [60] and its effects on the photodegradation of anthraquinone dyes in solution [38] and in epoxy resins [26] have been studied. The involvement of an electron transfer process in the photofading reaction to give the radical anion ($A^{-}\cdot$) was proposed. The authors suggested that from a technological point of view, such stabilisers could be applied as an aftertreatment.

Thomas *et al.* improved the lightfastness of dyeings of acid dyes or metal complex dyes on polyamide by treating them with a copper hydroxamate (**19**) before, during or after dyeing [61].



R, R_1 = aliphatic, aromatic or heterocyclic systems

(19)

Kirjanov and Bannigan similarly suggested the use of copper sulphonates, applied during or after dyeing, for acid dyes on nylon [62], and Rohr *et al.* also described a method for dyeing polyamide fibers with acid dyes in the presence of metal salts to improve the lightfastness [63].

Oda and Kitao proposed the use of nickel or zinc salts of 1-hydroxy-2-naphthoic acid and its derivatives as effective inhibitors of the photofading of indicator dyes in pressure- (or heat-) sensitive recording systems [64]. The use of metal (Co, Cu, Ni, Pd, Pt) organic sulphonates and sulphates have also been proposed as colour photographic image stabilisers [58]. Abdullah *et al.* demonstrated that lightfastness of azo naphthol-dyed jute fabrics can be increased by chelating the dyes with nickel sulphate [65].

Yagami *et al.* examined the interaction between acid dyes and a fluorescent whitening agent of the stilbene type in dye photofading on wool and also studied the effect of treatment with a nickel salt. It was found that Ni sulphate exerted a stabilising effect in the order C.I. Mordant Black 17 > C.I. Acid Reds 18 and 88. Protection of the fluorescent whitening agent by the dye followed the order C.I. Acid Red 88 > C.I. Acid Red 17 > C.I. Mordant Black 17 [66].

Nakazumi *et al.* studied the effects of nickel complexes on the photofading of coloured thin glass films. Cationic dyes used were triphenylmethane, phenoxazine and phenothiazine derivatives. They found that bis(*o,o'*-diethylphosphorodithiolato)nickel was the most effective in inhibiting the photofading of the thin glass film coloured with cationic dyes [67].

Naumova and Zaitsev demonstrated that the addition of *m*-nitroaniline and *m*-nitrophenol to certain disperse dyes increased their lightfastness on acetate and polyamide fibers [68] and Nomichi *et al.* described a method of similar effectiveness using $CuSO_4$ and NH_3 useful for automotive fabrics [69].

Sunada has suggested the use of poly(acrylic acid) as an aftertreatment of cationic dyed cellulosic fibers for improving lightfastness [70].

Carbamates [71], alkylamines [72,73] and quaternary ammonium compounds [74] have been found to increase the lightfastness of reactive dyes on cotton. For reactive dyes on wool, Inaoka suggested an aftertreatment with hydrazinoamides (**20**) [75].

$$Me_2NNHCONH(CH_2)_6NHCONHNMe_2$$

(20)

Kuchczynska was able to improve the fastness properties of direct and disperse dyes on polyester–cellulose blends using an aftertreatment with a copolymer of dicyanodiamide–formaldehyde to give a light and wash fast fabric with good crocking resistance [76]. Recently, Ooba *et al.* using ethoxylated polyethylenimine sulfate in the dyeing of chromed leather with anionic dyes, obtained higher colour yields and lightfastness [77].

Kaimori *et al.* obtained wool fabrics with ultrahigh lightfastness suitable for automobile interiors by treating wool with various phosphoric acid salts prior to reactive dyeing [78] and Yamada improved the lightfastness of cationically dyed *m*-aramid fibers to a similar high standard by using in the dyeing bath, *p*-methoxycinnamic acid [79].

Brazauskas *et al.* also claimed an improvement in the lightfastness of synthetic fibers dyed with disperse dyes by treating them with an aqueous solution of epichlorohydrin, urea and orthophosphoric acid [80].

6 NON-ADDITIVE APPROACHES TO IMPROVING THE LIGHTFASTNESS OF DYED POLYMERS

Many other approaches have been investigated for improving the lightfastness of dyed polymers which do not involve the use of additives, but rather attempt to modify the physical characteristics of the system. Whilst these approaches do not strictly fall into the scope of this review, for completeness some of the more significant developments are considered here.

One possibility for altering the photodegradation characteristics of a dye–polymer composite is to alter the physical situation of the dye by altering its intermolecular interaction characteristics. Thus the state of aggregation of the dye, the strength of binding to the polymer, and the location of the dye within the polymer can all influence the observed rate of photodegradation.

Sulphonated anthraquinone dyes are an important group of dyes for dyeing wool, silk and polyamide fibres that generally show good lightfastness (in general, between 5 and 6). According to early work of Giles, dyes with planar molecules sulphonated at only one end are surface active, whereas symmetrically sulphonated dyes are not, and the difference in surface activity of the two classes might be expected to influence their lightfastness properties [81].

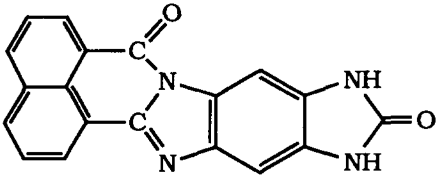
Giles *et al.* studied this effect with acid dyes on collodion, ethylmethylcellulose and gelatin films and found that symmetrically sulphonated dyes showed better lightfastness than the asymmetrical dyes [82]. Also, the light stability of a dye improved when the number of sulphonic groups in the dye molecule increased. These results seem to be related to the formation of aggregates.

Later, Shah and Jain reached similar conclusions for acid dyes on nylon 6.6 but they suggested that the increase in lightfastness of some monoazo dyes with increasingly number of sulphonic groups may be attributed to the increased strength of dye–fiber bonding [37]. However, Weatherall and Needles studied this effect on nylon and wool with six acid dyes and concluded that dye aggregation on wool did play an important role in lightfastness improvement [83].

Ueda reviewed the effect of terminal amino group content and dyebath pH on the light fastness of nylon 6 dyed with acid dyes and the effect of covalent bonds on the lightfastness of cellulose dyed with reactive dyes [84].

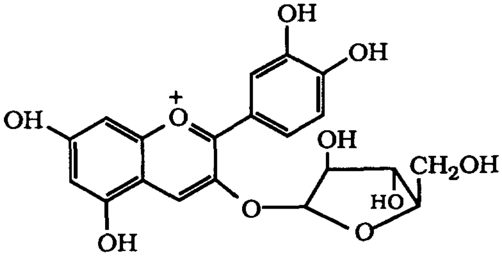
Akiyama *et al.* prepared an azine dye having excellent resistance to heat and light by treating the impure commercial dye with organic solvents and extracting the by-products [85]. The purified residue was much more stable to light and heat, when applied to nylon 6, than the initial commercial material.

Recently, new methods to improve the lightfastness of polymeric materials have been described such as structural modifications of polymers or mass dyeing of polyamide fibers. Kaul described how yellow polyamide fibers with improved lightfastness could be obtained by mass dyeing of polycaprolactam with heterocyclic dyes of type (**21**) [86] and Kato *et al.* obtained similar improvement for cationic dyes in aromatic polyamides [87], sulphonated aromatic dicarboxylic acid-modified polyamides and polyesters [88,89].

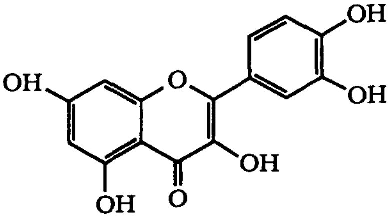


(21)

For producing dyed wool and Nylon with improved lightfastness the use of dyes based on lignin *p*-aminophenyl carbamate [90] have been claimed, as have anthocyanine dyes (**22**) and (**23**) for use on wool and silk [91–93].



(22)



(23)

When mixtures of two dyes are used on textiles the lightfastness of the combination is sometimes significantly lower than that of either of its constituent dyes, and the fading of one component is accelerated by the other [94]. This process is referred to as catalytic fading and the accepted mechanisms involve either excited state energy transfer from one dye to the other or generation of singlet oxygen by one of the dye components. A typical example is provided by the observations of Bhatt [95], who found that mixtures of Elite Fast Red 4B (**I**) and Lanasyn Yellow GLN (**II**) on wool gave lightfastness ratings as low as 1–2, whereas the individual dyes had lightfastness ratings of 5 and 7, respectively. Dye **II** was the catalytic component, accelerating the fading of dye **I**. The authors observed that they were not able to stop catalytic fading except by avoiding certain combinations of dyes or by eliminating impurities that might be involved.

Shah and Jain were able to improve the lightfastness of Lanasol dyes by including *n*-butanol in the dyebath during the reactive dyeing of nylon [96]. It seems that *n*-butanol facilitates deaggregation of the dye in solution, increases the diffusion rate and penetration of the dye through the substrate, and consequently enhances the lightfastness. Although aggregation of the dye molecules in the fibre is higher when applied from a bath without *n*-butanol, the lightfastness is lower. This is in contradiction to the view that aggregation increases the lightfastness [97]. However, according to the authors, the better results obtained with *n*-butanol are due to the higher diffusion rate of the dye within the substrate.

The same lightfastness improvement was found by these authors with the acid dyes C.I. Acid Orange 12, Acid Orange 10, Acid Red 111, Acid Red 131, Acid Red 88, Acid Red 13 and Acid Red 18 on nylon [98].

The resistance of acid dyes to photodegradation on nylon, was shown to be improved by the use of fluoropolymers [99,100], and Brodmann claimed a method to increase the lightfastness of non-ionic (or previously complexed) dyes when applied to nylon or polyester, taking place in an non-aqueous bath using an ester of high boiling point and achieved success in 33 of the 122 dyes studied [101].

Fukasawa *et al.* increased the lightfastness of metal complex dyes on Nylon 6 using zeolite-filled fibres ($>0.005\%$) which retain metals more ionizable than those in the dyes [102]. The dyeings with Lanasyn Yellow 2RL (copper complex), Lanasyn Bordeaux RL and Lanasyn Black RL (chromium complexes) gave lightfastness rating 4, versus 1–2 without the zeolite, and good strength retention and microbe resistance.

Valldeperas substituting sulphamic acid for H_2SO_4 in the dyeing process observed a decrease in the damage to the wool and, in some cases, an improvement in the lightfastness [103]. Ozone has been suggested as an after treatment of disperse dyed polyester for improved colour fastness [104].

Finally, a purely pragmatic approach for increasing the apparent lightfastness of dye mixtures in polymeric materials, especially textiles, is based on establishing dye combinations that provide compensation effects for colour variations in the absorption spectra of dyes during photofading. For example, Novoradovskii and Shtern have given appropriate data for mixtures of anthraquinone acid dyes which lead to an apparent enhancement of the lightfastness of dyed wool fibres [105].

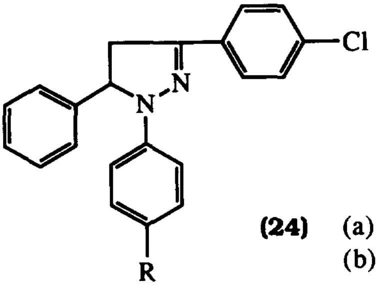
7 THE EFFECT OF FLUORESCENT BRIGHTENERS ON DYED POLYMERS

The most ubiquitous additives to accompany dyes on textile polymers are the *fluorescent brighteners.* Although these substances are not applied to polymers with the object of modifying photostability properties, nevertheless they can make an unintended but significant contribution to the observed lightfastness of a dyed polymer. Thus it is appropriate to consider optical brighteners as photochemically active additives and to examine the influence they can have on dye/polymer photostability.

Optical brighteners strongly absorb in the near UV, usually between 340 and 380 nm, and emit in the visible region between 400 and 440 nm. In most cases the presence of a brightener causes a decrease in the lightfastness of a dyed fibre [106].

The effect of optical brighteners on dye photodegradation has been studied by several authors. Reagan *et al.* examined the influence of five fluorescent agents on the photodegradation of acid dyes on silk and on the phototendering of the fibre [107]. They concluded that the rate of photodegradation was more dependent on the nature of the dye than on the optical brightener, and that the phototendering of the dyed fibre was directly related to the extent of dye photodegradation. The majority of the optical brighteners did not cause a marked change in the colour of the silk, except in the case of 4-methyl-7-(diethylamino)coumarin.

Yamada *et al.* demonstrated the catalytic degradation of 1,4-diaminoanthraquinone in the presence of oxygen and the pyrazoline fluorescent agent (**24a**) on irradiation of a solution of both with 366 nm light [108]. the catalytic agent being the coumarin. The retarding effect of the $^1O_2$ quencher 1,4-diazabicyclo[2.2.2]octane (DABCO), and chromatographic analysis of the photodegradation products confirmed that singlet oxygen was an intermediate in the process. The same catalytic effect of the fluorescent agent was observed in cellulose acetate films with a consequent increase in the rate of degradation of the dye. However, catalytic photodegradation could not be detected either in ethanol (which may be due to the shorter lifetime of $^1O_2$) or in nylon films (where $^1O_2$ may be quenched by amino groups).



(24) (a) R=SO_3Na
(b) R=H

A similar pyrazoline fluorescent agent (**24b**) was found to accelerate the fading of Methyl Violet in polyacrylonitrile film using light of wavelength 366 nm [109].

Shosenji *et al.* noted that the photodegradation of acid azo dyes was accelerated by the presence of optical brighteners of the pyrazoline type, e.g. (**24a**), and suggested that the initial process involved energy transfer from the triplet state of the pyrazoline to the dye [110].

Slizite *et al.* examined the effect of different types of optical brighteners on the photodegradation of several dyes applied to nylon [111]. They observed that the lightfastness of acid azo and anthraquinone dyes strongly decreased in the presence of optical brighteners, particularly with those of the pyrazoline type (Belofor SNPA), whereas the photochemical stability of reactive dyes was only slightly affected by optical brighteners of other types (Belofor KLA). The same authors observed, however, that in the case of metalised dyes, the photodegradation rate slightly decreased in the presence of optical brighteners, the most efficient being Vobital BVA.

Fluorescent brighteners can also, of course, have a direct photochemical effect on the polymer substrate in the absence of dyes, and this is best known in the case of wool. Thus optically whitened wool will yellow on exposure to light much faster than untreated wool. This is a photocatalytic process and the rate of yellowing of the polymer far exceeds the rate of photodegradation of the fluorescent brightener. Mechanistic aspects of the process have been reviewed by Nicholls [112].

Schäfer suggested that inorganic pigments such as barium sulfate or titanium dioxide applied together with fluorescent whitening agents onto bleached wool helped to retard the photoyellowing of the optically brightened wool [113].

8 CONCLUSIONS

It is evident from the sheer number of patents and research publications in the field of colorant/polymer photostabilisation that this is perceived to be an area of major technical importance. The versatility and ease of fabrication of a polymer are of little value if the durability of the polymer towards the rigours of our atmosphere cannot match that of more traditional materials. Thus the rewards to be gained from the economical stabilisation of polymers and their associated colorants are considerable, and research in this field is certain to continue unabated.

It is now clear that no polymer or colorant photodegrades by a single well defined mechanism, and similarly no photostabilising additive will exert its effect by a single process. These observations do of course make mechanistic investigations difficult, but with the increasing sophistication of instrumental techniques our knowledge of degradation and stabilisation mechanisms will become increasingly more exact in the future.

The economic push for stabilised colorant/polymer materials has resulted in many empirical approaches to the problem, which if anything have served to complicate the situation rather than clarify it. It is gratifying therefore that the most important technological advances in photostabilisers in recent years have originated from systematic mechanistic approaches, and future advances in photostabilisation are also most likely to originate from such strategies.

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