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New Perylene and Violanthrone Dyestuffs for Fluorescent Collectors

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ABSTRACT

The operating principle and possible applications of fluorescent collectors are described and some new yellow, red and blue dyestuffs derived from perylene are unveiled and their physical properties discussed. Studies of the photodecomposition mechanisms of these dyestuffs show that photostability is a very system-dependent parameter. Suggestions are made for improving the long-term stability.

1 INTRODUCTION

Fluorescent collectors consist of transparent plastic plates in which the fluorescent dyestuffs are incorporated. The principle of how fluorescent collectors function is outlined in Fig. 1. The incident light ray is absorbed by the dyestuff molecules and emitted as fluorescent light. The latter undergoes total reflection at the horizontal surfaces of the plate to a fairly large extent, such reflection varying with the refractive index of the plate material, and consequently reaches the edges, where it emerges in concentrated form. A fluorescent collector can therefore be thought of as a chemical lens.

A number of applications have been proposed[1] for this effect, which was first described by Keil[2] in 1969 and subsequently subjected to intensive study by Goetzberger and co-workers[3,4] and other teams.[5–7] The collected light can be converted into electricity by means of solar cells. Since it works even under low-level light conditions allowing the solar cell requirement to be

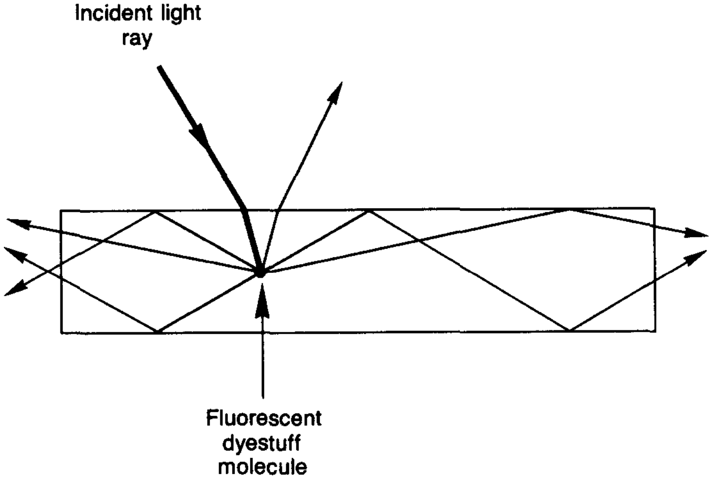


Fig. 1. Principle of the fluorescent collector.

reduced by up to 90%,[8] this system is very suitable for mains-independent power supply units in small electrical appliances, such as clocks,[9] charging equipment[10] or displays. The ability to concentrate light can also be exploited in illuminated signs, optical indicators,[11,12] drawing instruments,[13] light conductors, jewellery, leisure products and fluorescent displays.[14] Because of their Stokes shift, fluorescent dyestuffs can also be employed as wavelength converters, for example in scintillation detectors[15] and in sheeting for promoting plant growth.[16]

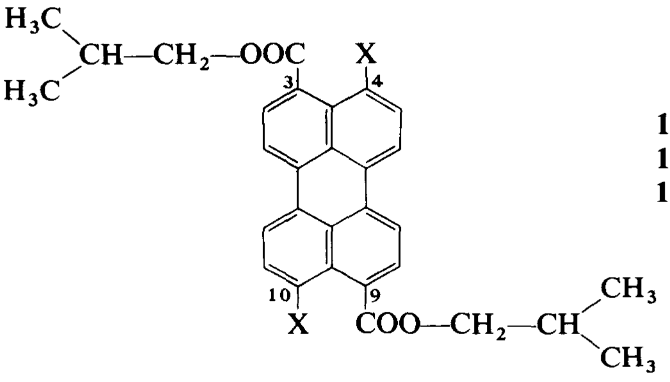
2 DYESTUFFS FOR USE IN FLUORESCENT COLLECTORS

These applications require dyestuffs which exhibit high fluorescence quantum yields, very good long-term photostability, large Stokes shifts and good processing properties in plastics systems, especially in the highly transparent and photochemically stable poly(methyl methacrylate) (PMMA).

2.1 Perylene dyestuffs

C.I. Solvent Green 5 (**1a**) is used as a fluorescent dyestuff on an industrial scale for colouring plastics, oils and resins.[17]

In spite of its moderate photostability in PMMA,[18] the purified form of this dyestuff has been recommended for manufacturing fluorescent collectors.[19] The reason for the low photostability possibly resides in the high reactivity of positions 4 and 10 towards electrophilic agents, and we



1a $X = H$
1b $X = CN$
1c $X = SO_2—C_6H_5$

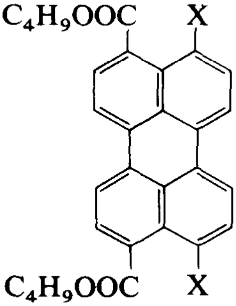
therefore synthesized perylene derivatives having additional acceptor groups at the 4- and 10-positions. Compound **1a** can readily be brominated in the 4- and 10-positions, and **1b** and **1c** can be prepared by nucleophilic replacement of the bromine atoms. With 3,4,9,10-tetrabromoperylene as the starting material, 3,4,9,10-tetracyanoperylene can be prepared by reaction with copper cyanide, but this compound is only moderately soluble in organic solvents.

Compound **1b**, in particular, exhibits outstanding properties for use in fluorescent collectors.[20]

2.1.1 *Properties of* ***1b***

λ_{max} for absorption (PMMA) = 474 nm, $\varepsilon(CHCl_3) = 48\,000$
λ_{max} for fluorescence (PMMA) = 508 nm
Quantum yield of fluorescence in $CHCl_3$: $\phi = 91\%$,

The additional cyano groups in **1b** hardly influence the position of the absorption and emission bands with respect to **1a**, but markedly increase the photostability. Whilst exposure to light (Xenotest®, Firma Heraeus, D-6450 Hanau) for 168 h reduces the extinction of **1a** in a PMMA test plate by 12%, the extinction of **1b** is reduced by only 4%. If the industrially available grade of 3,9-perylenedicarboxylic acid is used as starting material for the synthesis



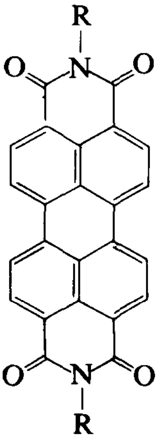
2a $X = H$
2b $X = CN$

instead of the pure grade, a product is obtained which also contains the positional isomer **2b** in addition to **1b**. This mixture of dyestuffs exhibits better solubility in media such as methyl methacrylate. One exponent of this class of dyestuffs is now commercially available (Lumogen® F-Dyes, BASF AG Ludwigshafen).

2.2 Perylimide dyestuffs of type 3

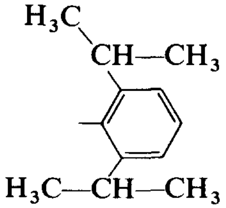
This group of compounds has been used for many years for colouring plastics materials. In the literature, reference is made, in particular, to their intense fluorescence and to their high degree of lightfastness in various polymer systems.[21] However, because of their limited solubility, the known perylimide dyestuffs were not suitable for use in fluorescent collectors. The moderate solubility is due to the planar structure of the molecule which facilitates the formation of crystals with high lattice energies. Many compounds of type **3** are even notable for an extraordinary low solubility in all common solvents and are therefore employed industrially as pigments for paints and plastics, an example being the derivative in which R = CH_3 (C.I. Pigment Red 179). The introduction of bulky radicals for R, in particular *ortho*-alkyl-substituted aromatics which are rotated by 90°C out of the plane of the molecule, makes it possible to decrease the crystal packing density. Such compounds, for example **3b** and **3c**, have good solubilities (Table 1).[22-25]

The compound **3b** was subjected to intensive studies in order to determine the long-term photostability. A PMMA plate coloured with this compound still exhibits 65% of the initial fluorescence after being subjected to outdoor weathering for 5½ years (Fraunhofer Institut für Solare Energiesysteme, Freiburg, pers. comm.).



3a R = $—C_7H_{15}$

3b R =



3c R =

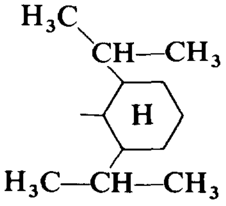


TABLE 1
Solubility Data

	3a	**3b**	**3c**	**4b**
Solubility in ethyl acetate at 20°C mg litre^{-1}	96	390	495	10000

2.2.1 Properties of ***3b***

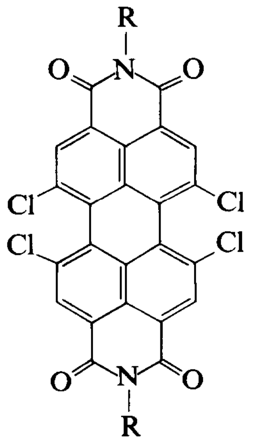
λ_{max} for absorption (PMMA) = 525 nm, $\varepsilon(CHCl_3) = 85\,000$
λ_{max} for fluorescence (PMMA) = 540 nm
Quantum yield of fluorescence in $CHCl_3$: $\phi = 100\%$

Despite the relatively small Stokes shift, which is characteristic of this group of compounds, some dyestuffs of this type are available commercially, not least because of their high photostabilities and their almost quantitative fluorescence quantum yields (Lumogen® F-Dyes, BASF AG, Ludwigshafen, FRG; Aldrich GmbH, FRG).

2.3 Substituted perylimide dyestuffs

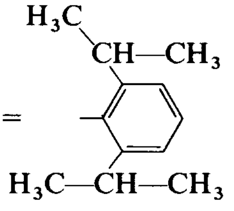
Perylimides are known to be capable of halogenation,^{26} but mixtures of compounds with various degrees of halogenation are obtained with the processes described in the patent literature. However, the use of specific conditions makes it possible to prepare pure 3,4,9,10-tetrachloroperylimides. Compound **4a** is obtained by chlorinating the *N*,*N*′-dibutylperylimide with sulphuryl chloride in nitrobenzene.^{27}

A comparison of X-ray structures of various perylimides shows that, in contrast to derivatives of type **3**, the molecules of **4a** in the lattice are no



4a = C_4H_9

4b =

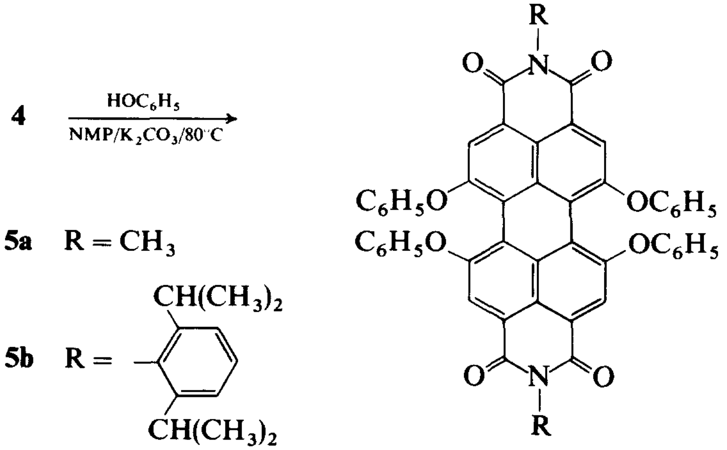


longer flat but have a distorted structure with the two halves of the perylene skeleton being twisted by 42° with respect to each other as a result of the strong repulsion of the peri-chlorine atoms (Hädecke, E. and Iden, R., BASF, unpublished).

There is no marked change in the spectral properties of the chlorinated compounds of type **4** compared with those of type **3**. The absorption maximum in $CHCl_3$ occurs at 524 nm, but the fluorescence undergoes a fairly strong bathochromic shift and its maximum now occurs at 551 nm, the vibrational structure of the emission band no longer being very pronounced. Although fluorescence quantum yields and photostabilities of the chlorinated compounds are in general somewhat lower than those of the unsubstituted perylimides (fluorescence quantum yield for **4a**: $\phi = 92\%$),[28] compounds of this type are recommended in the patent literature as dyestuffs for solar collectors because of their high solubility (Table 1) and good separation between absorption and emission.[19]

Compounds of type **4** are reactive at the chlorine positions towards nucleophilic agents. Exchange reactions have been performed in dipolar aprotic solvents with KF, CuCN, mercaptans, sulphinic acids, alcohols, phenols and amines.[28–30] In reactions with phenols, each of the four chlorine atoms can be successively exchanged by phenoxy radicals under suitably controlled conditions. These products exhibit particularly interesting properties. With the increasing degree of substitution the absorption band and also the fluorescence band are shifted bathochromically. In this manner, deep red dyestuffs of type **5** are obtained from the orange–yellow perylimides of type **4**.

The long-term stability of compounds of type **5** is good and similar to that of the compounds of group **3**. After 1·5 years of outdoor weathering of a



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PMMA plate coloured with **5b** the optical density dropped by 7% and the fluorescence by 10%. When the chlorine atoms were replaced by phenoxy radicals the solubility was tremendously increased, exceeding 100 g litre^{-1} in ethyl acetate at 20°C.

Compound **5b** even dissolves in petroleum ether and can be used to colour polyethylene films. Compounds of this type are now commercially available (Lumogen® F-Dyes, BASF AG Ludwigshafen, FRG).

*2.3.1 Properties of **5b***

λ_{max} for absorption (PMMA) = 578 nm, $\varepsilon(CHCl_3) = 44\,000$
λ_{max} for fluorescence (PMMA) = 613 nm
Quantum yield of fluorescence in $CHCl_3$: $\phi = 96\%$

The application of dyestuffs of type **5** in promoting the growth of green plants has been of special interest. In initial field trials using coloured sheeting it was possible to observe an increase in yield of up to 20% in the case of particular crops such as tomatoes, lettuce and kohlrabi.

2.4 Violanthrone and isoviolanthrone dyestuffs

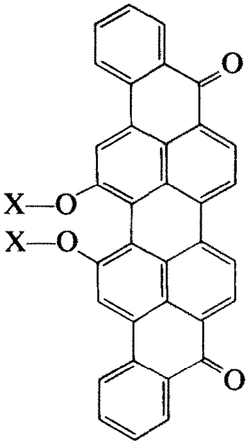
Violanthrones are vat dyestuffs which are frequently used for dyeing cotton fibres. Acylation of dihydroxyviolanthrone **6a** by dihydroxyisoviolanthrone **7a** with a large number of acid chlorides produces orange to red fluorescent dyestuffs which are notable for their high solubility and quantum yields of fluorescence of around 100%.[31]

*2.4.1 Properties of **6d***

λ_{max} for absorption (PMMA) = 578 nm, $\varepsilon(CHCl_3) = 53\,000$
λ_{max} for fluorescence (PMMA) = 615 nm
Quantum yield of fluorescence in $CHCl_3$: $\phi = 95\%$

The photostability of the new violanthrones and isoviolanthrones is dependent on the acyl radical used. Compound **6d** was found to be the most photostable of the derivatives of the hydroxyviolanthrone examined here; however, there is some tendency for the sulphonyl radical to split off under injection moulding conditions, i.e. at temperatures above 280°C. On exposure to light, compounds **6d** and **7b** form photoproducts which absorb at longer wavelengths, presumably as a result of a light-induced Fries rearrangement. Violanthrones are generally more lightfast than isoviolanthrones.

Alkylation of **6a** and **7a** produces blue fluorescent dyestuffs, some of which even emit in the infrared region. Dyestuffs of this type with long-wave



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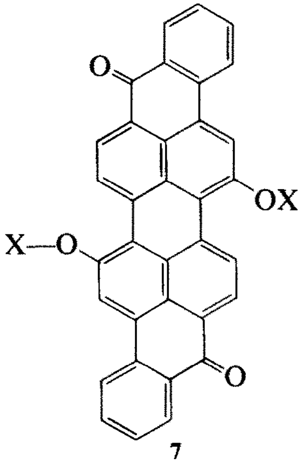

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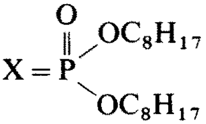
a $X = H$

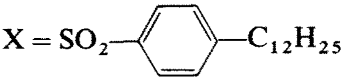
b $X = CO{-}C_{17}H_{35}$

c

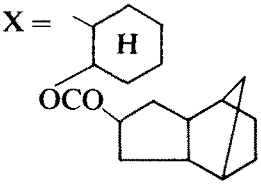


$X = P(=O)(OC_8H_{17})_2$

d



e



fluorescence are particularly attractive for use in fluorescent collectors.[1] The properties of the dyestuffs obtained depend on the nature of the alkyl radical, and it was found that dialkoxyisoviolanthrones containing very large alkyl radicals such as compounds **7e** have good photostabilities and high fluorescence quantum yields.

2.4.2 *Properties of 7e*

λ_{max} for absorption (PMMA) = 610 nm, $\varepsilon(CHCl_3) = 63\,000$
λ_{max} for fluorescence (PMMA) = 685 nm
Quantum yield of fluorescence in $CHCl_3$: $\phi = 92\%$
Solubility in ethyl acetate at 20°C: 864 mg litre^{-1}

An explanation of this high photostability might be that the photoreactive carbonyl groups in the chromophore are shielded by the bulky branched alkyl radicals.

3 PHOTOSTABILITY OF FLUORESCENT DYESTUFFS AND FLUORESCENT COLLECTORS

The remarkably good photostability of the three dyestuffs **3b**, **6d** and **7e** in PMMA is not an inherent property of these dyestuffs but is very critically dependent on the matrix surrounding them.[28] In PMMA samples doped with these dyestuffs it was found that prolonged exposure to light caused not only a reduction in the absorption of the dyestuff but also the simultaneous growth of additional absorption peaks at longer wavelengths (see Fig. 2(a) and (b)); the latter caused a reabsorption of part of the fluorescent light and therefore led to a marked reduction in the light conduction efficiency of a collector plate.

3.1 The effect of the ambient atmosphere

On exposure to solar radiation, colourless PMMA exhibits a well-known yellowing effect (which is due to the appearance of photoproducts); this is largely independent of the ambient atmosphere (O_2 or N_2).

Figure 2(a) and (b) shows the absorption spectra of PMMA platelets 3 mm thick which had been doped with **3b** before and after exposure to light (Suntest®) for 11 days in an oxygen and a nitrogen atmosphere respectively.

For the UV range and also for the particularly troublesome additional absorption peaks at long wavelengths a greater increase is found in the nitrogen atmosphere than in the oxygen atmosphere. Nevertheless, the overall decomposition of the dyestuff in oxygen is greater than in nitrogen (greater decrease in the extinction at 526 nm of PMMA coloured with **3b**).

Figure 3 shows the increase in the additional absorption peaks at long wavelengths with time: as the exposure time is extended, there is a continuous increase in the peaks at 610 nm and 700 nm.

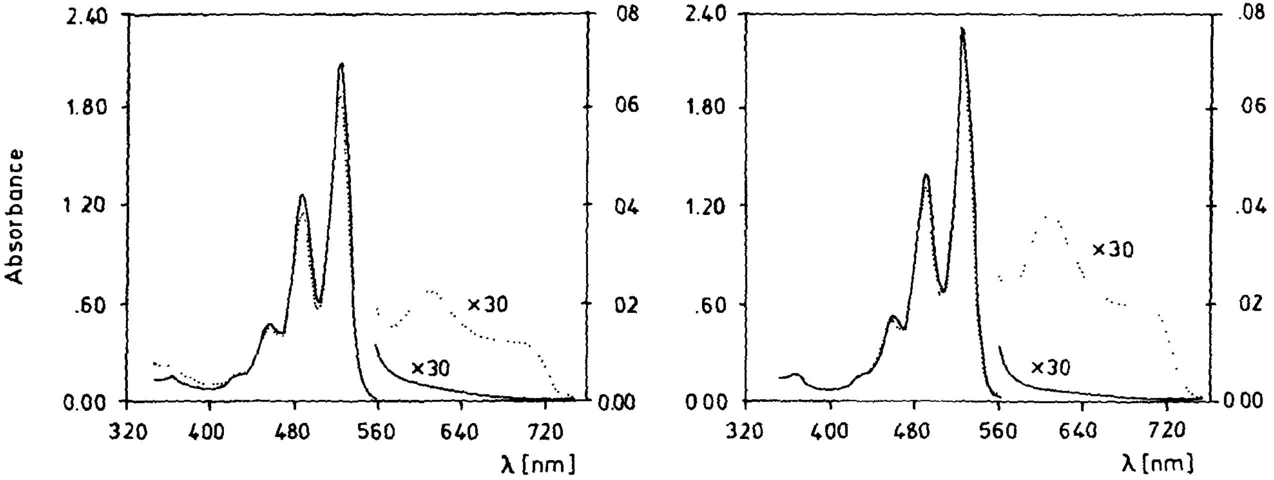
If these samples are kept in the dark, the peaks at 610 and 700 nm do in fact disappear with time, but there remains a troublesome additional absorption around 560 nm. This relaxation proceeds much more rapidly in an oxygen atmosphere than in a nitrogen atmosphere.[29]

3.2 Effect of UV light

Many examples[32] are known in which a relatively small part of the spectrum in the UV-B range has a dominant effect on the photodecomposition of a system. Therefore the influence of the spectrum of the illumination source on the photostability was studied.

Figure 4 shows the change in the spectrum of PMMA doped with **3b** when exposed to light without UV-B, i.e. using a 3-mm-thick edge-filter, WG345 (Schott).

Comparison of Fig. 4 with Fig. 2(a) and (b) reveals that if the UV-B is



(a) (b)

Fig. 2. Exposure of PMMA doped with **3b** to light; (a) in oxygen; (b) in a nitrogen atmosphere. —— Before exposure; - - - - after exposure.

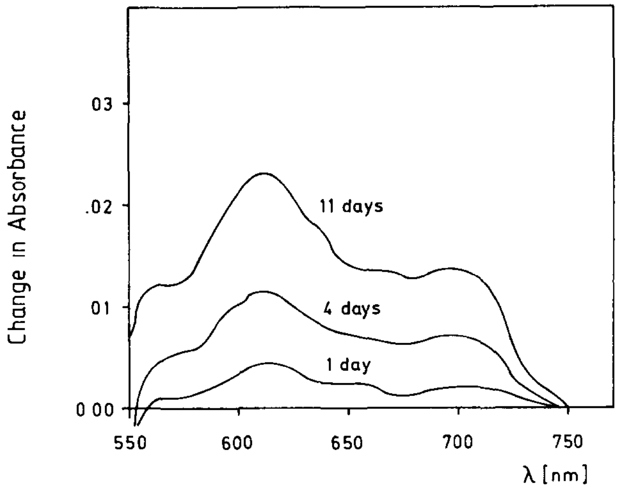


Fig. 3. Compound **3b** in PMMA; increase in the photodegradation products with long-wave absorption after exposure to light (including UV-B) for 1, 4 and 11 days.

filtered out, only a slight decomposition of the dyestuff occurs and there is no increase in the UV absorption peaks (PMMA yellowing) and in the additional absorption peaks at long wavelengths.

Experiments with a series of cut-off filters, ranging from WG 290 to GG 420 (Schott), revealed that photostability is achieved with WG 345 which cannot be significantly improved any further by additional filtering.

Very similar effects are found in irradiation experiments with PMMA platelets which have been doped with **6d**. Here again a substantial

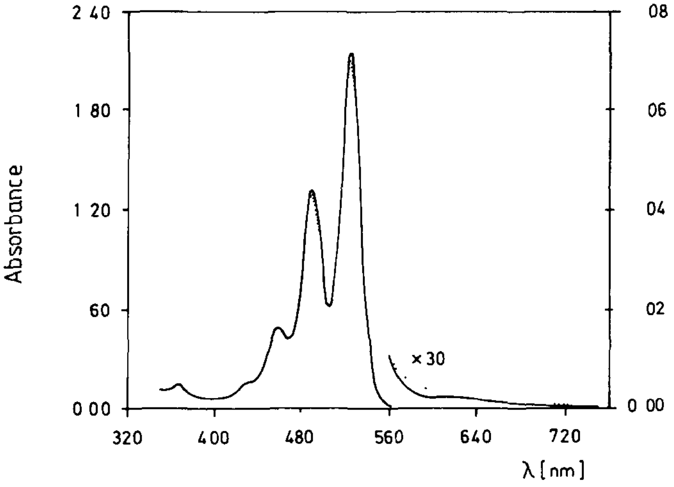


Fig. 4. Exposure of PMMA coloured with **3b** to light with UV-B light excluded [using a WG 345 edge-filter (Schott) 3 mm thick] in air. —— Before exposure; ---- after exposure.

improvement in the photostability of the system is achieved by filtering out the UV light up to 345 nm.

In practice the same effect can be achieved by using a commercially available UV-absorber.

3.3 Effect of some of the PMMA polymerization parameters

There are indications that the structure and concentration of the free-radical initiator and also the PMMA plate manufacturing process have a significant effect on the photostability of fluorescent collectors.[29]

Oxygen is known[33–35] to inhibit the polymerization process of methyl methacrylate and at the same time to be incorporated in the polymer chains. The latter then contain peroxy or hydroperoxy groups which are thermally unstable and UV-sensitive structural elements which may destroy the dyestuff directly and through the agency of possible secondary products.

The presence of oxygen during the polymerization process has been found to accelerate the subsequent decomposition of the dyestuff and also to intensify the increase in the addition absorption peaks at long wavelengths. This oxygen effect is closely related to the sensitivity to UV-B described above.

3.4 Mechanism studies

All attempts to isolate and identify the photoproducts formed from the PMMA by means of gel permeation or adsorption chromatography and by reprecipitation or extraction were unsuccessful due to the small quantities, since the photochemical conversion is extremely low even with prolonged exposure to light (quantum yield $<10^{-7}$) and the products formed again undergo further decomposition in their turn.

Model experiments were used to determine which photophysical primary processes may be relevant in the dyestuffs under consideration.

3.4.1 Electron transfer reactions

Molecules in their electronically excited S_1 states are generally easier to reduce or to oxidize than molecules in the ground state.[36,37] The radicals formed in a primary process of this type might then be converted in further reactions to form photoproducts.

Photoreduction. An electron donor D is able to supply an electron to an electronically excited dyestuff molecule ${}^1F^*$:

$$ {}^1F^* + {}^1D \rightarrow {}^2F^- + {}^2D^+ $$

and convert it into a radical anion ${}^2D^-$ with a relatively long life.[38,39]

TABLE 2

Half-Value Concentrations (mol litre^{-1}) for the Dyestuff/Reducing Agent Pairs

	Reducing agent		
Dyestuff	*DEA in* $CHCl_3$	ChH_2 *in DMF*	*TMB in* $CHCl_3$
3b	0·019	0·041	0·061
6d	0·017	0·034	0·43
7e	0·037	0·131	Very large

The quenching of fluorescence in solution was used for a quantitative study of the photoreduction of **3b**, **6d** and **7c** by the fairly weak reducing agent 1,3,5-trimethoxybenzene (TMB), the moderately strong reducing agent hydroquinone (ChH_2) and the fairly strong reducing agent *N*,*N*-diethylaniline (DEA). The values of the half-value concentrations C_h determined from Stern–Volmer plots are listed in Table 2.

In the case of **3b**, a marked photoreduction is obtained even with the weak TMB, while the fairly strong DEA is required for **6d** and even for **7e** (see Refs 38 and 39 for the dependence on the redox potential of the reducing agent).

Experiments on the quenching of fluorescence in the PMMA matrix yielded similar results.[29]

Photo-oxidation. In addition to photoreduction of the dyestuff, photo-oxidation is also possible as a photophysical primary process of a multistage decomposition mechanism.[40]

Raising an electron from the HOMO to the LUMO makes it considerably easier to oxidize an excited dyestuff molecule $^1F^*$.[41,42]

$$^1F^* + A \rightarrow {}^2F^+ + {}^2A^-$$

Experiments on the quenching of fluorescence in $CHCl_3$ were carried out on **6d** and **7e** using chloranil as the oxidizing agent. From the Stern–Volmer plots we obtained the following half-value concentrations: $C_h = 0{\cdot}021$ mol litre^{-1} for **6d** and $C_h = 0{\cdot}012$ mol litre^{-1} for **7e**. The violanthrone **7e** is markedly more sensitive to oxidizing agents than to reducing agents. These values show that photo-oxidation has to be considered in discussing the photodegradation of violanthrones and isoviolanthrones.

These results make it clear that the luminosity and the photostability of a fluorescent collector depend to a large extent on the concentration of those impurities or additives which are capable of acting as electron donors or acceptors.

3.4.2 Singlet oxygen

Model experiments in solvents indicated that singlet oxygen does not significantly accelerate the photodecomposition of the dyestuffs **3b**, **6d** and **7e**.

4 SUMMARY

The ambitious aim of developing fluorescent dyestuffs with long-term stability in PMMA was achieved by synthesizing novel perylene and violanthrone dyestuffs.

From the results it emerges that the photostability of the system can be markedly improved by adopting a number of precautions, viz. excluding oxygen during polymerization, avoiding impurities and troublesome additives, and also by filtering out UV light up to at least 345 nm.

There is therefore no longer anything to prevent a wider application of fluorescent collectors.

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