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NEW DAYLIGHT FLUORESCENT PIGMENTS

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SUMMARY

The synthesis and properties of a series of plastosoluble daylight fluorescent pigments based on benzanthrone, 1-azabenzanthrone, 14H-[2,1,9-mna]*thioxanthene-14-one and its 5-aza analogue are reported.*

1. INTRODUCTION

It is known that fluorescent pigments are used in several technical fields,[1,2] e.g. printing inks, paints, the colouration of moulded plastics (particularly polystyrene, polymethylmethacrylate, polycarbonate), the dyeing of man-made fabrics (especially polyester), industrial safety applications (safety clothing, warning flags), advertising and for the manufacture of small articles (i.e. bottle caps, detergent bottles, toys, lighters, etc.). The industrial manufacture of these pigments began after the Second World War and after an initial slow growth considerable progress has been made in the last two decades.

The tinctorial power of a fluorescent pigment is higher than that predictable from the absorbance value due to the phenomenon by which an excited molecule, after deactivation through loss of vibrational energy on reaching the lowest vibrational level of the first excited singlet state, undergoes a radiating transition to a higher vibrational level of the ground state rather than a radiationless process to the lowest ground state. While for most of organic molecules the phenomenon of vibrational relaxation from the excited state with loss of energy by collision with neighbouring molecules is much more rapid than photoemission (i.e. the molecule reaches its

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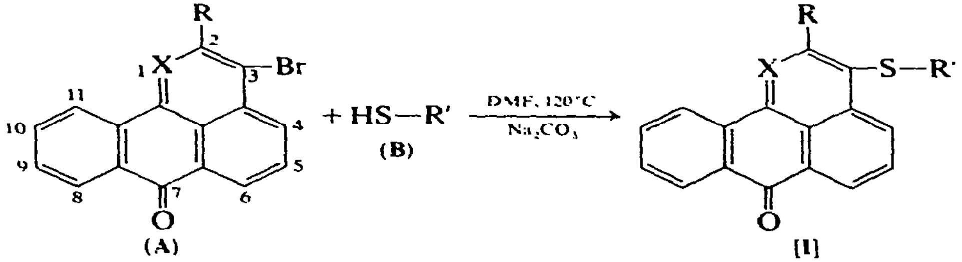
ground state without emitting radiation), the emission of photons of lower frequency is a rather exceptional characteristic.

No fixed rules for fluorescence can be drawn. It is favoured by ring closure because of the contribution of heteroatoms (N, O, S) to π-electron systems. A rigid structure, which avoids dissipation of vibrational energy, is also favourable. Thus the search for new fluorescent pigments is of interest for both theoretical and practical purposes. We report here some new products with fluorescence properties and their application results arising as part of our development programme[3] designed to produce new fluorescent pigments of technical nutrient.

The products synthesized are derived from the following two structures:

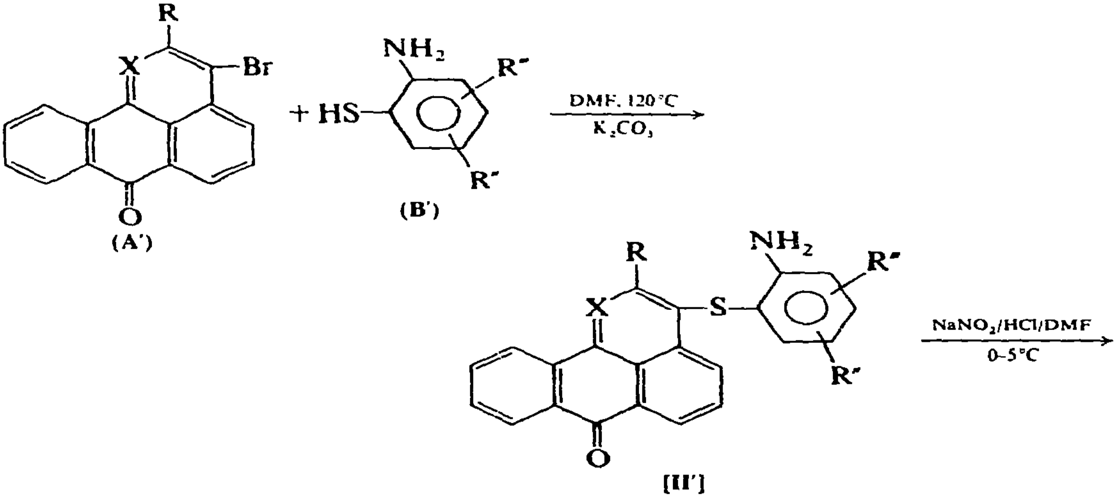
[**I**], which is obtained by condensation of 3-bromobenzanthrone or 3-bromo-1-azabenzanthrone (**A**) with thiophenols (**B**), according to the scheme:

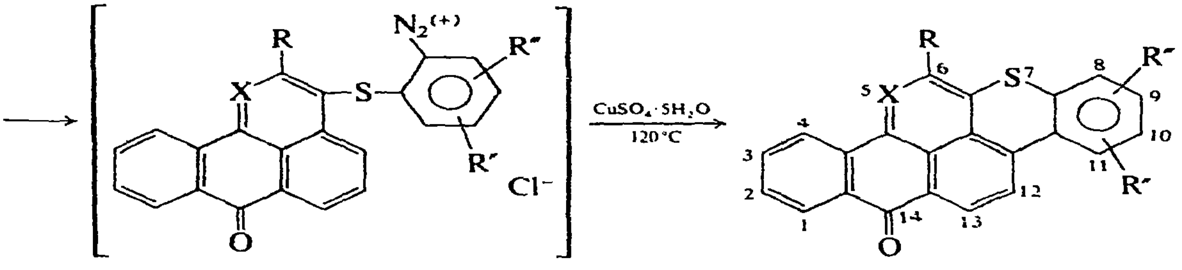


where X = CH, N; R = H, O—alkyl; R' = aromatic, heteroaromatic, or aliphatic radical.

Products [**Ia–u**] are reported in Table 1.

[**II**], which is obtained by intramolecular cyclization of derivatives [**II'**], starting from **A'** and **B'** according to the scheme:





[II]

where X = CH, N; R = H, O—alkyl; R'', R''' = H, alkyl, halogen, O—alkyl.

The final step of the synthesis of derivatives [II'] is a Pschorr cyclization,[4] which allows the approach to the ring [II] based on the skeleton of 14*H*-anthra [2,1,9-*mna*]thioxanthene-14-one or of its 5-aza analogue.

The products of this series are reported in Table 2 (pigments [IIa–l]).

Compound [IIa] is a known pigment synthesized according to the procedure illustrated in section 2 (involving, in spite of a previous patent,[5] a much lower quantity of $CuSO_4 \cdot 5H_2O$) and is included in Table 2 for comparison.

2. EXPERIMENTAL

Melting points were determined using a Tottoli apparatus and were uncorrected.

Visible absorption spectra were recorded on a Pye–Unicam SP 1800 spectrophotometer using DMF as a solvent. Fluorescence spectra were recorded on polystyrene plates 40 mm × 20 mm × 2 mm containing 0·02% of pigment, using a Pretema FS4 spectrophotometer with the monochromator positioned between the specimen and the detector, and compared with the spectra obtained by a Pye–Unicam SP8-100 spectrophotometer having a monochromator between the light source and the specimen. The light source was a xenon lamp simulating the standard illuminant D65. The two superimposed spectra showed the wavelength and the intensity of fluorescent emission. The absorption maxima were also obtained from the two curves.

The specimens were prepared as follows: 0·02 g of the dye was dispersed and homogenized with 100 g of polystyrene (PS) or poly(methyl methacrylate) (PMMA) in a rotating drum for 18 h at 110°C. The material obtained was extruded at 190–220°C, granulated, dried and moulded by injection press at 220–300°C in 100 mm × 40 mm × 2 mm plates.

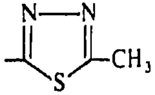
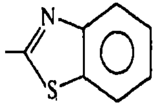
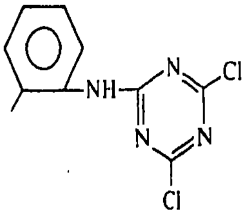
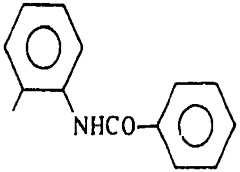
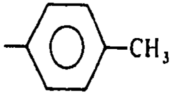
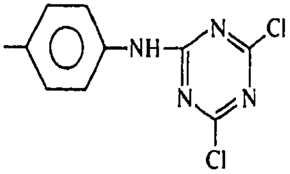
Fastness properties were measured according to the UNI norms.

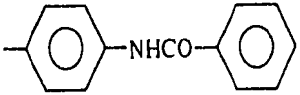
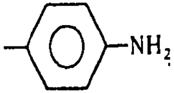
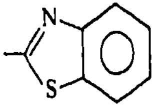
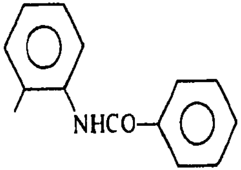
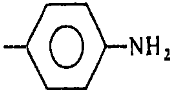
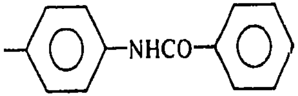
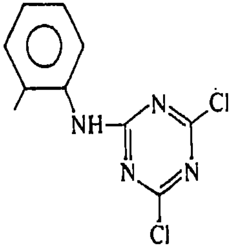
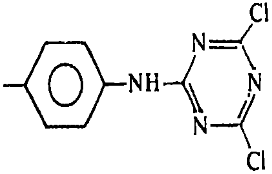
2.1. *Preparation of products* [I]—*general method*

Product of general formula **A** (0·02 mol) was reacted with 0·03 mol thiophenols of general formula **B** in 50 ml DMF in the presence of 0·033 mol sodium carbonate by

TABLE 1

PIGMENTS [I]

Pigment	*X*	*R*	*R′*	*M.p. (°C)*	*Crystn. solvent*	*Yield (%)*	*Formula molecular wt*	*Analysis: calc. (%) found (%)*	λ_{max} *(nm) (DMF)*
[I a]	CH	H		244–6	*o*-DCB	—	$C_{20}H_{13}N_2OS_2$ 361·47	66·46(C) 3·62(H) 7·76(N) 17·74(S) 18·02(S)	400
[I b]	CH	H		191–3	DMF	72	$C_{24}H_{13}NOS_2$ 395·51	72·88(C) 3·31(H) 3·54(N) 16·21(S) 73·12(C) 3·41(H) 3·45(N) 15·95(S)	400
[I c]	CH	H		—	*o*-DCB	—	$C_{26}H_{14}Cl_2N_4OS$ 501·41	62·28(C) 2·81(H) 11·17(N) 6·39(S) 62·31(C) 2·71(H) 10·94(N) 6·28(S)	420
[I d]	CH	H		225–7	DMF	—	$C_{30}H_{19}NO_2S$ 457·55	78·75(C) 4·18(H) 3·06(N) 7·01(S) 78·92(C) 4·05(H) 3·22(N) 6·94(S)	420
[I e]	CH	H		228–30	DMF	75	$C_{24}H_{16}OS$ 352·46	81·79(C) 4·58(H) 9·10(N) 81·92(C) 4·49(H) 8·85(N)	430
[I f]	CH	H		237–9	*o*-DCB	—	$C_{26}H_{14}Cl_2N_4OS$ 501·41	62·28(C) 2·81(H) 11·17(N) 6·39(S) 67·41(C) 2·80(H) 10·85(N) 6·40(S)	440

[Ig]	CH	H		241–3	o-DCB	—	$C_{30}H_{19}NO_2S$ 457·56	78·75(C) 4·18(H) 3·06(N) 7·02(S) 78·54(C) 4·17(H) 3·15(N) 6·93(S)	440
[Ih]	N	OCH_3		250–2	DMF	—	$C_{23}H_{16}N_2O_2S$ 384·46	71·85(C) 4·19(H) 7·29(N) 8·94(S) 71·90(C) 3·99(H) 7·25(N) 8·62(S)	450
[Ii]	N	OCH_3		225–7	DMF	—	$C_{24}H_{14}N_2O_2S_2$ 426·52	67·58(C) 3·31(H) 6·61(N) 15·04(S) 67·54(C) 3·42(H) 6·65(N) 15·00(S)	450
[Ij]	N	OCH_3		—	o-DCB	—	$C_{30}H_{20}N_2O_3S$ 488·57	73·75(C) 4·13(H) 5·73(N) 6·56(S) 73·49(C) 4·34(H) 5·67(N) 6·50(S)	460
[Ik]	CH	H		—	—	—	$C_{23}H_{15}NOS$ 353·45	78·16(C) 4·28(H) 3·97(N) 9·08(S) 78·51(C) 4·18(H) 3·61(N) 8·94(S)	460
[Il]	N	OCH_3		281–3	DMF	—	$C_{30}H_{20}N_2O_3S$ 488·57	73·75(C) 4·13(H) 5·73(N) 6·56(S) 74·02(C) 4·45(H) 5·62(N) 6·84(S)	460
[Im]	N	OCH_3		—	o-DCB	—	$C_{26}H_{15}Cl_2N_5O_2S$ 532·43	58·65(C) 2·84(H) 13·15(N) 6·02(S) 58·24(C) 2·95(H) 12·77(N) 6·06(S)	460
[In]	N	OCH_3		284–6	o-DCB	—	$C_{26}H_{15}Cl_2N_5O_2S$ 532·43	58·65(C) 2·84(H) 13·15(N) 6·02(S) 59·11(C) 3·21(H) 12·72(N) 6·44(S)	460

(continued)

TABLE 1—*contd.*

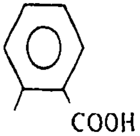
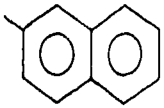
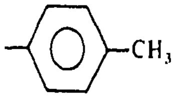
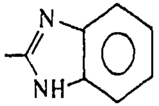
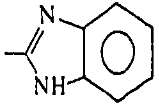
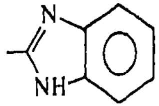
Pigment	*X*	*R*	*R′*	*M.p. (°C)*	*Crystn. solvent*	*Yield (%)*	*Formula molecular wt*	*Analysis: calc. (%) found (%)*	*λ*
[Io]	N	OCH_3		—	DMF	78	$C_{24}H_{15}NO_4S$ 413·45	69·72(C) 3·66(H) 3·39(N) 7·76(S) 69·35(C) 9·72(H) 3·57(N) 7·64(S)	460
[Ip]	N	OCH_3	$—CH_2COOH$	228·9	CH_3COOH	78·3	$C_{19}H_{13}NO_4S$ 351·39	64·94(C) 3·73(H) 3·99(N) 9·12(S) 65·13(C) 3·75(H) 4·12(N) 9·01(S)	460
[Iq]	N	OCH_3		—	DMF	45	$C_{27}H_{17}NO_2S$ 419·51	77·30(C) 4·08(H) 3·34(N) 7·64(S) 77·71(C) 4·32(H) 3·02(N) 7·35(S)	460
[Ir]	N	OCH_3		—	—	71	$C_{24}H_{17}NO_2S$ 383·47	75·17(C) 4·47(H) 3·65(N) 8·36(S) 74·82(C) 4·60(H) 3·56(N) 8·19(S)	460
[Is]	CH	H		>330	*o*-DCB	—	$C_{24}H_{14}N_2OS$ 378·46	76·16(C) 3·73(H) 7·41(N) 8·47(S) 75·84(C) 3·62(H) 7·71(N) 8·64(S)	470
[It]	CH	OCH_3		>330	*o*-DCB	74	$C_{25}H_{16}N_2O_2S$ 408·48	73·51(C) 3·95(H) 6·86(N) 7·85(S) 73·12(C) 3·84(H) 6·92(N) 7·93(S)	490
[Iu]	N	OCH_3		>330	*o*-DCB	50	$C_{24}H_{15}N_3O_2S$ 409·47	70·40(C) 3·69(H) 10·26(N) 7·83(S) 70·63(C) 3·55(H) 10·07(N) 7·90(S)	510

TABLE 2

PIGMENTS [II]

Pigment	*X*	*R*	*R″*	*R‴*	*M.p.* (°C)	*Crystn. solvent*	*Yield* (%)	*Formula molecular wt*	*Analysis: calc.* (%) *found* (%)	λ_{max} (*nm*) (*DMF*)
[IIa]	CH	H	H	H	300–303	*o*-DCB	—	$C_{23}H_{12}OS$ 336·41	82·12(C) 3·59(H) 9·53(N) 81·84(C) 3·88(H) 9·50(N)	510
[IIb]	N	H	H	H	320	*o*-DCB	61·5	$C_{22}H_{11}NOS$ 337·40	78·32(C) 3·29(H) 4·15(N) 9·50(S) 77·98(C) 3·35(H) 4·36(N) 9·61(S)	520
[IIc]	CH	H	9-OC_2H_5	H	246–8	*o*-DCB	—	$C_{25}H_{16}O_2S$ 380·47	78·92(C) 4·24(H) 8·43(N) 78·67(C) 4·05(H) 8·25(N)	520
[IId]	CH	OCH_3	9-Cl	11-CH_3	318–320	*o*-DCB	—	$C_{25}H_{16}ClO_2S$ 414·93	72·19(C) 3·88(H) 8·52(Cl) 7·71(S) 71·88(C) 3·53(H) 8·19(Cl) 7·75(S)	530
[IIe]	CH	OC_2H_4OH	H	H	310–312	*o*-DCB	63	$C_{25}H_{16}O_3S$ 396·47	75·74(C) 4·07(H) 8·09(S) 75·38(C) 4·19(H) 8·14(S)	540
[IIf]	CH	OCH_3	9-OC_2H_5	H	294–296	*o*-DCB	60	$C_{26}H_{18}O_3S$ 410·50	76·07(C) 4·42(H) 7·81(S) 76·41(C) 4·62(H) 7·47(S)	546
[IIg]	CH	OCH_3	H	H	≥320	*o*-DCB	64	$C_{24}H_{14}O_2S$ 366·44	78·66(C) 3·85(H) 8·75(S) 78·32(C) 3·71(H) 8·95(S)	546
[IIh]	N	OCH_3	H	H	316–318	*o*-DCB	68	$C_{23}H_{13}NO_2S$ 367·43	75·18(C) 3·57(H) 3·81(N) 8·73(S) 74·94(C) 3·68(H) 3·78(N) 8·91(S)	564
[IIi]	N	OCH_3	9-Cl	H	> 320	*o*-DCB	48	$C_{23}H_{12}ClNO_2S$ 401·88	8·82(Cl) 7·98(S) 8·54(Cl) 8·21(S)	560
[IIj]	N	OCH_3	9-Cl	11-CH_3	> 320	*o*-DCB	41	$C_{24}H_{14}ClNO_2S$ 415·91	8·52(Cl) 7·71(S) 8·61(Cl) 7·48(S)	568
[IIk]	N	$O(CH_2)_3CH_3$	H	H	268–270	*o*-DCB	—	$C_{26}H_{19}NO_2S$ 409·51	76·26(C) 4·68(H) 3·42(N) 7·83(S) 75·94(C) 4·38(H) 3·61(N) 8·00(S)	568
[IIl]	N	OCH_3	9-OC_2H_5	H	285–287	*o*-DCB	—	$C_{26}H_{17}NO_3S$ 423·50	73·74(C) 4·05(H) 3·31(N) 7·57(S) 74·01(C) 4·04(H) 3·35(N) 7·81(S)	570

refluxing for 2 h. On cooling, pigment [**I**] precipitated. After filtration and washing with DMF it was crystallized from DMF or *o*-dichlorobenzene (*o*-DCB) (see Table 1) and dried. Yields of crystallized products ranged from 40 to 80% based on the bromo derivative (A).

2.2. *Preparation of products* [**II**]—*general method*

The condensation step to intermediates [**II′**] was carried out as above. After crystallization and drying [**II′**] (0·01 mol) was dispersed in 50 ml DMF, the solution obtained was heated at 80 °C and kept at this temperature for 30 min, cooled at 0–5 °C, acidified with 10–15 ml of 36% HCl and diazotized by adding 0·01 mol $NaNO_2$ in 5 ml water with stirring for 30 min.

After 2 h at 0–5 °C, the temperature was raised to 25 °C. The mass was then treated with 0·04 g $CuSO_4 \cdot 5H_2O$, heated to 110 °C and kept at this temperature for 3 h. After cooling, filtration, washing with DMF and hot water, drying and crystallization from DMF or *o*-dichlorobenzene (see Table 2) pigments [**II**] were obtained in a yield ranging from 40 to 80% based on the intermediate [**II′**].

3. RESULTS AND DISCUSSION

3.1. *Absorption and fluorescence spectra*

Tables 1 and 2 report, together with the formulae of synthesized products, elemental analyses and absorption maxima in DMF. The wavelengths of these maxima are only indicative because the spectra, determined using a normal UV—visible spectrophotometer, are the resultant of fluorescence and normal colour; but some useful conclusions can be reached from the data obtained:

(*a*) The open-chain thioethers of Table 1 have absorption wavelength maxima ranging from 400 to 510 nm and therefore have colours ranging from greenish-yellow to orange (this corresponds to visual observation).

(*b*) Introduction of a methoxy-group into the 2-position of the benzanthrone ring gives rise to a bathochromic shift from yellow to orange (see pigments [**I s**] and [**I t**]); a further bathochromic shift is observed by substituting the group CH in [**I t**] by an N atom (see pigment [**I u**]).

(*c*) The shift towards orange is therefore favoured by the aza substitution in the 1-position and by the methoxy substitution in the 2-position; analogous indications are obtained by comparing [**I i**] with [**I b**] and [**I j**] with [**I d**].

Other considerations follow:

(*d*) The *S*-heteroaromatic group in the 3-position (pigment [**I u**]) is bathochromic with respect to the *S*-aromatic group in the same position (pigment [**I r**]).

(*e*) The latter is bathochromic with respect to the *S*-aliphatic group (pigment [**I** p]).

(*f*) S-benzimidazolyl group (pigments [**I** u] and [**I** s]) is bathochromic in comparison with the *S*-benzothiazolyl group (pigments [**I** i] and [**I** b]).

Table 2 concerning the polycondensed derivatives [**II**], shows a bathochromic shift taking place caused by aza substitution in the 1-position of the 14*H*-anthra[2,1,9-*mna*]thioxanthene-14-one structure ($X = N$ instead of $X = CH$, see pigments [**II** g] and [**II** a]) and methoxy substitution in the 6-position (OCH_3 instead of H: see pigments [**II** g] and [**II** h] in comparison with [**II** a] and [**II** b]).

Colours of the pigments in Table 2 range from red to violet. Together with those in Table 1 they cover a very large field of the visible spectrum (see also Tables 3 and 4).

For some selected pigments the fluorescence maxima were also determined by the instrumental method indicated in the experimental section employing specimens of PS 2 mm thick with the pigment incorporated. In Table 5 are summarized the fluorescence maxima and the corresponding emission intensities. The contribution of fluorescence emission is about 10–15 % for the four pigments selected ([**I** s], [**II** a], [**II** g], [**II** h]) at pigment concentration 0·02 %. It is important to note that for the four selected products the absorption maximum measured in DMF coincides with the absorption maximum recorded according to the above method. The coincidence demonstrates that for these four products of the series there is no fluorescence emission in the range of absorption maxima.

TABLE 3
PIGMENTS [**I**]: COLOUR IN PMMA AND LIGHTFASTNESS

Pigment	*Colour in PMMA*	*Lightfastness*[a]
[**I** a]	Greenish-yellow	2–3
[**I** b]	Greenish-yellow	2
[**I** c]	Greenish-yellow	2–3
[**I** d]	Greenish-yellow	4
[**I** e]	Greenish-yellow	3–4
[**I** f]	Greenish-yellow	2
[**I** g]	Greenish-yellow	3–4
[**I** h]	Yellow	5
[**I** i]	Yellow	5–6
[**I** j]	Yellow	6
[**I** k]	Yellow	5–6
[**I** l]	Yellow	6
[**I** m]	Yellow	5–6
[**I** n]	Yellowish-brown	3–4
[**I** o]	Yellow	5–6
[**I** p]	Yellow	2–3
[**I** q]	Yellow	5–6
[**I** r]	Yellow	4–5
[**I** s]	Yellow	4–5
[**I** t]	Orange	4–5
[**I** u]	Orange	6–7

[a] According to ISO standards.

TABLE 4
PIGMENTS [II]: COLOUR IN PMMA AND LIGHTFASTNESS

Pigment	*Colour in PMMA*	*Lightfastness*[a]
[II a]	Orange	5–6
[II b]	Orange	5–6
[II c]	Orange	6
[II d]	Red	6–7
[II e]	Violet-red	6–7
[II f]	Violet-red	6–7
[II g]	Violet-red	6–7
[II h]	Violet	6–7
[II i]	Violet	4
[II j]	Violet	5
[II k]	Violet	6–7
[II l]	Violet	6–7

[a] According to ISO standards.

3.2. *Tinctorial and fastness properties*

The fluorescent pigments described above show very bright shades and high tinctorial strength especially on polyester, particularly the products of Table 2 whose shades range from red to violet for pigments [II]. Lightfastness is, however, unsatisfactory. On the other hand when incorporated in plastic materials (PS, PMMA) the pigments show lightfastness ranging from good to excellent (Table 4).

Shades of the pigmented articles are practically identical for both PS and PMMA, as are the fluorescence effects. In Table 6 lightfastness of some pigments incorporated in different plastic materials—PS crystals, shock-resistant PS, shock-resistant PS + TiO_2, acrylonitrile–butadiene–styrene copolymer (ABS)—is illustrated.

It may be seen that lightfastness is greatly influenced by the chemical structure and by the plastic material employed. ABS generally affords better lightfastness than other materials, except in the cases of pigments [I r] and [I s]. All the pigments shown have good thermostability characteristics in the different substrates at moulding temperatures ($\sim$280 °C).

TABLE 5
ABSORPTION AND EMISSION SPECTRA OF PIGMENTS APPLIED IN PS

Pigment	*Absorption* λ_{max} *(nm)*	*Fluorescence emission* λ_{max} *(nm)*	*Fluorescence intensity* (%)
[I s]	470	536	14·5
[II a]	512	596	12·5
[II g]	540	620	12
[II n]	560	641	11·5

TABLE 6
LIGHTFASTNESS[a] OF SOME PIGMENTS [I] AND [II] APPLIED IN VARIOUS MATERIALS

Pigment	*PS crystals*	*Shock-resistant PS*	*Shock-resistant PS + TiO_2*	*ABS*
[**I i**]	1–2	1–2	—	4
[**I m**]	1–2	1–2	—	5
[**I o**]	2	1–2	—	4–5
[**I q**]	2	2–3	—	4–5
[**I r**]	3	2–3	2	2
[**I s**]	4	3	2	2
[**I u**]	3	5	2–3	3
[**II a**]	5	5–6	3	5
[**II g**]	5	6	3	5–6
[**II h**]	3	6	4	6
[**II e**]	2–3	5–6	3–4	4–5

[a] According to ISO standards.

4. CONCLUSIONS

In addition to the known compound [**II a**], various new interesting pigments have been found to associate pleasant fluorescence effects, good lightfastness and thermal stability when incorporated in PS, PMMA and ABS both in the absence or in the presence of opacifier.

The products are readily accessible considering that they are derived from 3-bromobenzanthrone, a usual intermediate in the synthesis of vat dyes, or from 2-hydroxybenzanthrone now easily accessible either according to the synthesis described in ref. 6 or from 2-hydroxy-1-azabenzanthrone which is also available from the procedures described in refs. 7 or 8.

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